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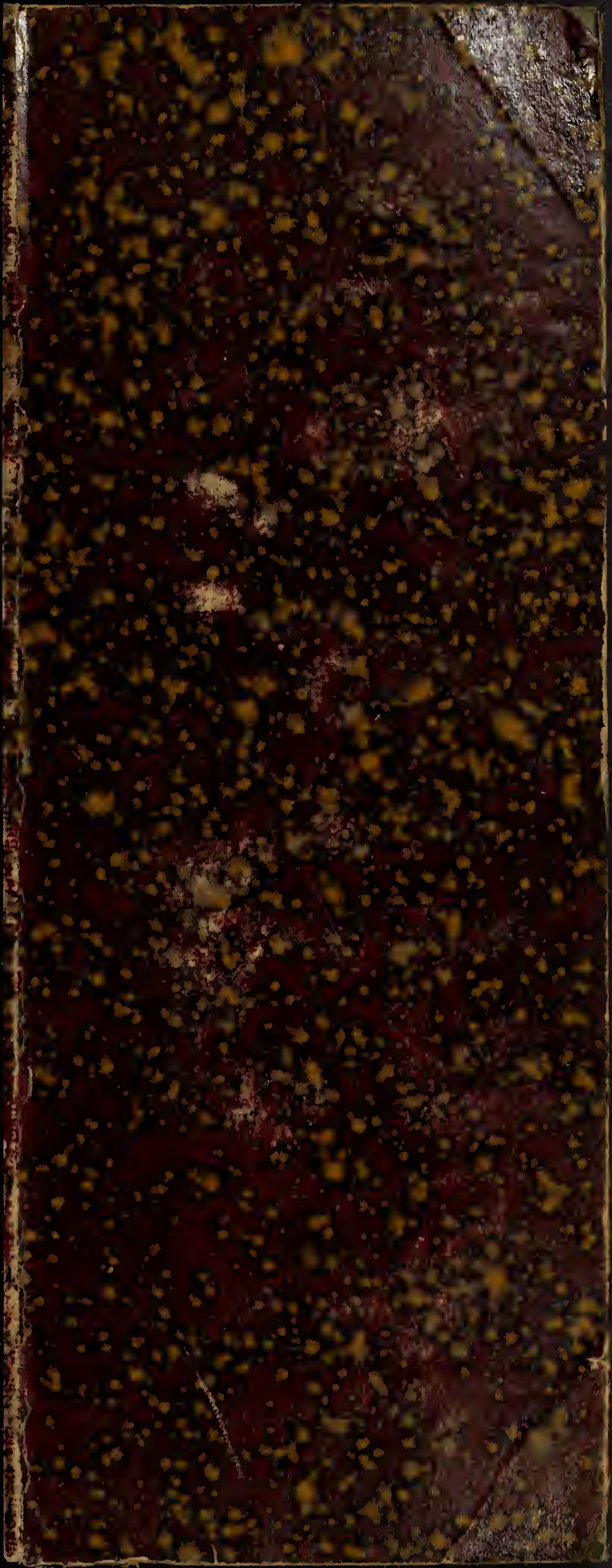

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THE DIELECTRIC CONSTANTS OF ICE DOWN TO LIQUID AIR TEMPERATURES

BY

OSCAR ALAN RANDOLPH

B. S. Missouri School of Mines, 1911

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

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IN

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June 5 1913

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

OSCAR ALAN RANDOLPH

ENTITLED THE DIELECTRIC CONSTANTS OF ICE DOWN TO LIQUID AIR TEMPERATURES

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF SCIENCE

A. P. Carman
In Charge of Major Work

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on
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CONTENTS

PART I

		Page
I	Early History	1
II	Theories of the Dielectric	4
III	The Clausius-Mosotti Relation	7
IV	The Application to Artificial Dielectrics	9
V	The Relation as Applied to Gases and Vapors	11
VI	The Relation as Applied to Liquids and Solids	13
VII	The Dielectric Constant of Mixtures	15
VIII	The Dielectric Constant and the Change of State	16
IX	The Dielectric Constant and Strain	17
X	The Effect of Frequency on the Dielectric Constant	19
XI	Work done on Ice and Water	21
XII	The Dielectric Constant and Temperature	25
XIII	Other Observations on the Dielectric Constant	28

PART II

I	Methods Tested Out in this Investigation	29
II	Description of Apparatus	32
III	Platinizing the Condenser	39
IV	Diagram of Apparatus	41
V	Manipulation	42
VI	Explanation of Experimental Data and Curves	44
VII	Experimental Data and Curves	46
VIII	Discussion of Results	75

PART I

THEORETICAL AND HISTORICAL

I EARLY HISTORY

Previous to the year 1748, the medium through which electric forces act was considered as relatively unimportant. Benjamin Franklin[1] in 1748 startled the scientific world by the experiment of the dissectable leyden jar. This experiment called attention to the fact that the electrical energy resided in the medium surrounding the charged conductors and not in the conductors themselves. In other words the conductors are only important because they are voids in the insulating medium and the layers of tinfoil in a leyden jar serve only to short circuit simultaneously the whole of the two layers of the strained medium.

A little later, in 1777, Coulomb using the torsion balance, proved that Newton's law of inverse squares holds for the cases of electric and magnetic attraction and repulsion. He and others of his time however, assumed action at a distance and thought that these forces, like gravitational forces, are independent of the medium through which they act.

It remained for Faraday to correct this error. He imagined that electric attraction and repulsion was propagated by means of the molecular action "of the contiguous particles of the insulating medium". According to this idea the medium should have an effect on electrostatic forces and this medium through or across which the forces act, he called the dielectric. Further, as it was necessary to compare dielectrics with one another, he defined the ratio of the capacity of a condenser when X is the dielectric to the capacity of the

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[1] Benjamin Franklin, Letters on Electricity.

condenser when air is the dielectric as the "specific inductive capacity" of the substance X. This ratio is now more generally known as the "dielectric constant". Using this definition and working with two spherical condensers exactly alike and with a proof plane and torsion balance in order to measure potentials, he found the dielectric constant of shellac and sulphur to be different from unity. This discovery called for a revision of Coulomb's law, which must now include a term dependent upon the medium; viz., $F = \frac{e_1 e_2}{k r^2}$, k being the dielectric constant. Pushing his observations further, Faraday noted that in many instances there was a slow creep of the electric charge into the dielectric medium and hence realized that for many substances the dielectric constant depends upon the time of charge.

It is true that Cavendish anticipated both Coulomb and Faraday by a number of years. He had worked out a more precise proof than that of Coulomb for the inverse square law. He had also found by the use of a pith ball electrometer, that coated plates of glass and paraffin contained more charge than was to be expected from the thickness and area of the plates when compared to air. Unfortunately his results were hidden from scientists until published by J. Clerk Maxwell[2] in 1879.

Since the time of Faraday considerable work has been done on dielectric constants. This constant has been found to be greater than unity for all dielectrics if a vacuum instead of air is used as the standard medium[*]. Although this is independent of the electric

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[2] J. Clerk Maxwell, The Works of Henry Cavendish.

[*] Assuming the dielectric constant of a vacuum as unity that of ordinary atmospheric air is 1.00059, a number which for most practical purposes can still be considered as unity.

intensity, it has been found to depend upon the time of charge, for solid and liquid dielectrics as well as upon the temperature and mechanical strain to which the dielectric is subjected. In the case of certain crystals (calcite, sulphur, etc.) it has been found to vary according to the optical axis along which it is measured.

II THEORIES OF THE DIELECTRIC

Faraday pictured the dielectric medium filled with lines of force. To him these lines had a real existence and possessed certain definite properties. They tended to shorten in their longitudinal direction, they repelled each other sideways and they began at positively charged bodies and ended on negatively charged ones. The electric charges were merely the free ends of the strained medium. In order to account for these lines he reasoned (from analogy, with the Poisson Theory of Magnetism) that the dielectric might be composed of particles of a conductor imbedded in an insulating medium. He says, "If the space around a charged globe were filled with a mixture of an insulating dielectric, as oil of turpentine or air and small globular conductors, as shot, the latter being a little distance from one another so as to be insulated, then these would in their condition and action resemble what I consider to be the condition and action of the particles of the insulating dielectric itself. If the globe were charged, these little conductors would all be polar; if the globe were discharged they would all return to their normal state, to be polarized again upon recharging the globe[3]". This assumption was investigated mathematically by Mosotti who applied a method previously used by Poisson[4]. A little later Clausius extended the mathematical treatment and completed the foundation of what is now known as the Clausius-Mosotti theory.

The great advance however, was made by Maxwell who used the idea of changing dielectric polarization to explain all electrical pheno-

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[3] Michael Faraday, Experimental Researches, Vol. I, Sec. 1679.

[4] S. D. Poisson, Sur la théorie du magnetisme Mém. de l'Acad. francaice, Vol. 5, (1882) and Vol. 6(1823).

mena. He clothed Faraday's theory of lines of force in mathematical terms and thought of a dielectric subject to electric forces as analagous to a medium strained by mechanical forces. In order to carry out this analogy the term "electrical displacement" was needed. In ordinary mechanics, the energy necessary to produce a displacement x in an elastic medium is $\frac{1}{2}Fx$. In electrostatics the energy per unit volume of a dielectric is $\frac{1}{8\pi} f^2k$, where f is the electric intensity and k the dielectric constant. Comparing the two formulae it is seen that the quantity $\frac{fk}{4\pi}$ corresponds to the mechanical displacement and hence is called the electrical displacement. Using this idea Maxwell has defined the dielectric constant as "the ratio of the displacement in any dielectric to the displacement in a vacuum due to the same electromotive force".

The more recent theories of the dielectric retain all the essentials of the Faraday-Maxwell conception but differ as to the nature of the electric displacement, which they claim to be a displacement of electrons. Typical of these may be taken the theory of H.A.Lorentz. To use his words, "In a ponderable dielectric there can (likewise) be a motion of electrons. Indeed though we shall think of each of them as having a definite position of equilibrium, we shall not suppose them to be wholly immovable. They can be displaced by an electric force exerted by the ether, which we conceive to penetrate all ponderable matter, a point to which we shall soon have to revert. Now, however, the displacement will immediately give rise to a new force by which the particle is pulled back towards its original position and which we may therefore appropriately distinguish by the name of elastic force. The motion of the electrons in non-conducting bodies, such as glass and sulphur, kept by the elastic force within certain

bounds, together with the change of the dielectric displacement in the ether itself constitutes what Maxwell called the displacement current. A substance in which the electrons are shifted to new positions is said to be electrically polarized."[5]

General References

Faraday, Experimental Researches, Vol. I.

Maxwell, Electricity and Magnetism, Vol. I. (Sec. 60 in particular)

Campbell, Modern Electrical Theory, p. 48, et. seq.

Tunzelmann, A Treatise on Electrical Theory.

Larmor, Aether and Matter, p. 252, et. seq.

Lorentz, The Theory of Electrons.

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[5] H. A. Lorentz, The Theory of Electrons, Columbia University Adams Fund for Physical Research Publications, Vol. 2, p. 8, (1909)

III THE CLAUSIUS MOSOTTI RELATION

One of the results of the work of Clausius[6] on the Mosotti theory of the dielectric was an interesting relation between the dielectric constant and the relative volume* of the conducting molecules. In the derivation of this it was assumed that the conducting molecules were spherical and that their relative volume was a small fraction of the total volume of the dielectric. The relation was first stated in the forms

$$k = \frac{1 + 2u}{1 - u} \quad - - - - - \qquad (1)$$

and

$$u = \frac{k - 1}{k + 2} \quad - - - - - \qquad (2)$$

where u is the relative volume of the conducting molecules and k is the dielectric constant. This last equation can be thrown into another form by dividing both sides by d, the density of the dielectric. This gives

$$\frac{u}{d} = \frac{1}{d}\,\frac{k - 1}{k + 2} \quad - - - - \qquad (3)$$

a formula first derived by Lorentz[7]. In the latter form $\frac{u}{d}$ is the real specific volume of the conducting molecules, or in other words, the volume occupied by the conducting molecules in one gram of the dielectric. Hence, it is a constant independent of the state of aggregation, the temperature or the pressure. Equation (3) may be put into a somewhat different form by use of the relation known as Maxwell's law. This is generally stated, as follows; the square of the refractive index of a substance for very long light waves is equal

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[6] Clausius, Mech. Wärmetheorie, Vol. 2, p. 94, (1874).

*By relative volume is meant the ratio of the volume of the conducting molecules to the volume of the dielectric.

[7] H. A. Lorentz, Wied, Ann., Vol. 9, p. 641, (1880).

to the dielectric constant of the substance. It is usually written $k = n^2$. When this value of k is inserted in (3) the result is,

$$\frac{n^2 - 1}{(n^2+2)d} = C \qquad (4)$$

where C is the constant $\frac{u}{d}$. This formula was derived almost simultaneously by Lorentz[8] and Lorenz[9].

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[8] H. A. Lorentz, loc. cit.

[9] L. Lorenz, Wied, Ann., Vol. 11, p. 77, (1880).

IV THE APPLICATION TO ARTIFICIAL DIELECTRICS

The Clausius-Mosotti relation has been tested by many authors by making an artificial dielectric such as was pictured by Faraday. Millikan[10] has done this using an emulsion of water in benzol-chloroform mixture of specific gravity unity. The water was so much better conducting than the benzol-chloroform that the globules of it could be considered as the conducting molecules while the benzol-chloroform itself formed the dielectric proper. In experiments of this kind the ether is not assumed as the insulating material and the formula $k = k' \frac{1 + 2u}{1 - u}$ must be used. Here k is the dielectric constant of the mixture, k' that of the insulating material and u (the relative volume of the conducting molecules) is the number of cubic centimeters of conductor divided by the total volume of the mixture. Millikan found the agreement of $\frac{k}{k'} = \frac{1 + 2u}{1 - u}$ to be from 0.2 to 1.2% which was as good as could be expected from the experimental method used. A little later Beaulard[11] tested the above expression using definite mixtures of copper filings and paraffin. The agreement obtained by this investigator was not as good as that obtained by Millikan, but ranged from 0.7 to 4.0%. A possible reason for his results not checking closer might be given that he did not fulfill the requirement of spherical molecules. More ideal conditions were obtained by Hlawati[12] who performed the experiment using various mixtures of finely divided mercury in lanolin and other similar fats.

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[10] R. Millikan, Wied, Ann., Vol. 60, p. 376, (1897).

[11] F. Beaulard, Comptes Rendus, Vol. 129, p. 149, (1899).

[12] F. Hlawati, Akad. Wiss. Wien. Sitz. Ber., Vol. 110, Series 2a, p. 454, (1901).

He obtained a good agreement and only in one case did the error amount to as much as 1%.

V THE RELATION AS APPLIED TO GASES AND VAPOURS

The relation when applied to gases and vapors generally leads to satisfactory results. In these cases since we are dealing with substances of dielectric constant nearly equal to unity it is frequently written $\frac{k - 1}{3d} = C$ or $\frac{k - 1}{d} = C_1$ which amounts to saying that k - 1 is proportional to the density. Boltzmann[13], who did the pioneer work in this field, found the relation to hold with great accuracy for gases at constant temperature and varying pressures. He was followed by Klemenčič[14] who verified the former's work and extended the experimental evidence so that it included the vapors of the low boiling point liquids as well. The work of these two investigators, however, only covered pressures up to about one atmosphere. Recently Tangl [15], working with air, hydrogen and nitrogen with pressures as high as 100 atmospheres finds the agreement between the observed and calculated values of k to be as good as could be desired. On the other hand an Italian physicist, A. Occhialini[16], in an investigation carried on with air, finds a slow increase of the constant C with increasing temperatures. Lebedew[17] has studied the relation in regard to the change of state of several vapors and has found an agreement which while of a remarkable degree of magnitude is not as exact is to be experimentally expected. Bädeker[18] has carried the

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[13] L. Boltzmann, Akad. Wiss. Wien. Sitz. Ber., Series 2, Vol. 69, p. 795, (1874).

[14] I. Klemenčič, Akad. Wiss. Wien, Sitz. Ber. Series 2, Vol. 91, p. 712, (1885).

[15] K. Tangl, Ann. d. Physik, Series 4, Vol. 26, p. 59, (1908)

[16] A. Occhialini, Acad. Lincei. Atti., p. 603, (1905).

[17] P. Lebedew, Wied. Ann., Vol. 44, p. 288, (1891)

[18] K. Bädeker, Zeit. f. Phys. Chem., Vol. 36, p. 305, (1901).

work on gases and vapors to higher temperatures and has studied the relation as applied to the vapors of higher boiling point liquids; but was not able to obtain nearly so good agreement as was found by the previous investigators. However, he makes the interesting observation that with increase of temperature Maxwell's law tends to be obeyed. He states further that this law and the Clausius-Mosotti relation go hand in hand; that is, when Maxwell's law fails to apply with changes of temperature the same is true of the Clausius-Mosotti relation. The work has been extended to lower temperatures by Linde[19] who studied the relation for easily liquifiable gases in the liquid state. He found that the relation did not hold for these cases.

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[19] L. Linde, Wied. Ann., Vol. 56, p. 546, (1895).

VI THE RELATION AS APPLIED TO LIQUIDS AND SOLIDS

As previously stated the agreement in the case of liquids and solids in general, has not been good. Lebedew[20] found fair agreement for benzol, vaseline, alcohol and water, by calculating k and comparing it with the dielectric constant of these substances measured at various temperatures by Palaz[21], Fuchs[22] and Rosa[23]. A careful investigation was carried out by Heerwagen[24] in 1893 on the chang of the dielectric constant of water with temperature. His work was confined to the range from 4° to 20.75°C and his results show that in the interval from 4° to 10°C, the Clausius-Mosotti constant varies markedly. Ether has proved a most notable exception. Tangl[25] has found that for the range 20° - 193.3°C (the critical temperature) the constant decreases as the temperature increases, the maximum deviation being as much as 17%. He also found that for benzol, toluol, metaxylol, carbon disulphide and chloroform there was a marked variation, in some cases the deviation being negative and in others positive. Eversheim[26] has investigated liquid sulphur dioxide and ethyl chloride and finds that the "constant" for these substances increases with rising temperature. Ortvay[27] has studied the effect of

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[20] P. Lebedew, loc. cit.

[21] A. Palaz, Jour. de Physique, Series 2, Vol. 5, p. 370, (1885).

[22] V. Fuchs, Akad. Wiss. Wien. Sitz. Ber., Series 2,Vol.98, p.1240 (1889).

[23] E. Rosa, Phil. Mag., Series 5, Vol. 31, p. 88, (1891).

[24] F. Heerwagen, Wied. Ann., Vol. 49, p. 276, (1893).

[25] K. Tangl, Ann. d. Physik, Series 4, Vol. 10, p. 748, (1903).

[26] P. Eversheim, Ann. d. Physik, Series 4, Vol. 8, p. 539, (1902)

[27] R. Ortvay, Ann. d. Physik, Series 4, Vol. 36, p.1, (1911).

pressure and has worked as high as 500 kg./cm^2. His results show that the Clausius-Mosotti relation does not hold for ether and benzene under the conditions of the experiment. The "constant" in both cases decreased with the higher pressures. For ether the decrease was 1.3%, and for benzene 1.17% of the original value. For the calculation of the dielectric constant at any pressure, the following empirical formula is given,

$$k_p = k(1 + ap + bp^2)$$

where a and b are constants, a being positive and b negative. His research covers, besides ether and benzene, toluene, xylene, carbon disulphide, chloroform, liquid paraffin, petroleum ether and castor oil. In every case the dielectric constant increased with pressure but the increments decreased.

VII DIELECTRIC CONSTANT OF MIXTURES

Considerable work has been done on the dielectric constant of mixtures and solutions resulting in a large number of empirical formulae. Among the most interesting of these researches is one by Philip[28] on liquid mixtures. He finds the dielectric constant of ether to be 4.3 and that of chloroform to be 4.8 while mixtures of the two give values which are, in general, above 5.0. The research also covered a large number of solutions of the various alcohols in benzene and toluol. The formula $\frac{\sqrt{k}-1}{d} = C$ was found to hold better than the Clausius-Mosotti relation, however the agreement was not good for either formula. Tangl[29] in his paper on the dielectric constant of mixtures of hydrogen, nitrogen and air at high pressures gives the following formula,

$$k_m - 1 = (k_1 - 1)(k_2 - 1) ,$$

where k_m is the dielectric constant of the mixture and k_1 and k_2 is the dielectric constant of the two components at their respective partial pressures. Ten systems of solid mixtures each having napthalene as one component, have been studied by Rudolphi[30]. The $\sqrt{k}$ formula for mixtures given above was found not to hold for these systems.

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[28] J. C. Philip, Zeit. f. Phys. Chem., Vol. 24, p. 18, (1897).

[29] K. Tangl, loc. cit., Ann. d. Physik, Series 4, Vol. 26, p. 59, (1908).

[30] E. Rudolphi, Zeit. f. Phys. Chem., Vol. 66, p. 705, (1909).

VIII THE DIELECTRIC CONSTANT AND CHANGE OF STATE

The dielectric constant of a few organic substances has been studied with regard to the change of state. Abegg and Seitz[31] have investigated several alcohols, p-azoxyanisol and nitro-benzene. They find that all these substances show an enormous decrease in the dielectric capacity upon solidification, and that the visible change of the alcohols from the glassy to the crystalline solid condition takes place without noticeable change in this constant. Another observer, J. Hattwich[32] determined the values for paraffin, phenanthrene and napthalene for the temperature range 15° - 190°C. His results show that no general rule can be given for their behavior. Napthalene shows a minimum at its melting point, phenanthrene a maximum at 10° above the melting point and paraffin has a maximum while it is still in a pasty condition (at 30°C). The values for liquid carbon dioxide and its saturated vapor have been found to approach each other as the temperature is raised. This has been noted by Verain[33] from whom the following results are quoted.

Temperature	Dielectric Constant of Liquid CO_2	Dielectric Constant of Saturated CO_2 Vapor
0°C	1.58	1.04
10°	1.54	1.07
20°	1.48	1.11
30°	1.32	1.20
31.4°	1.25	1.25

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[31] R. Abegg and W. Seitz, Zeit. f. Phys. Chem., Vol. 29, pp 242 and 491, (1899).

[32] J. Hattwich, Akad. Wiss. Wien., Sitz. Ber. Series 2a, Vol.117, p. 903, (1908).

[33] L. Verain, Comptes Rendus, Vol. 154, p. 345, (1912).

IX THE DIELECTRIC CONSTANT AND STRAIN

Investigations as to the effect of strain on the dielectric constant are difficult as the change to be measured is small. Ercolini has obtained an increase in the value for glass as the load increased while Corbino, Panichi and Wüllner and Wien[34] have obtained a decrease. As the method of calculation and experimentation of the first three has been questioned and as Wüllner and Wien have used the most sensitive method, their paper should perhaps be accepted as decisive. Their conclusions are as follows: The change of the dielectric constant of glass under tension at right angles to the lines of force is in general negative. The change is smallest for Thüringian glass where it scarcely exceeded the error of observation, is larger for Jena glass and is the largest in flint glass.

India rubber has been studied by Corbino and Cannizzo and more recently by Schiller[35].

The results here are in agreement both ascribing a decrease of the dielectric constant with increasing tension.

A subject very intimately related to the above is that of electrostriction or the study of the deformations produced by electric stresses. The researches of More[36] and the later investigation by Adams and Heaps[37] show that the present theory is erroneous and that the deformations generally observed are due to heating. Further the

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[34] A. Wüllner and M. Wien, Ann. d. Physik, Series 4, Vol. 11, p. 619, (1903).

[35] L. Schiller, Ann. d. Physik, Series 4, Vol. 35, p. 931, (1911).

[36] L. T. More, Electrical World and Engineer, Vol. 43, p.127, (1904).

[37] E. P. Adams and C. W. Heaps, Phil. Mag., Vol. 24, p. 507, (1912).

deformation that should be looked for is only a small fraction of that which has generally been expected.

Adams and Heaps have also studied the effect of twist on the dielectric constant of glass and find that it is without result.

X THE EFFECT OF FREQUENCY ON THE DIELECTRIC CONSTANT

The refractive index n in Maxwell's law[38], $k = n^2$, is the refractive index of the dielectric for infinitely long waves. This is generally calculated from the observed index by means of Cauchy's formula for dispersion,

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + - - - - - .$$

If after determining the constants A, B, C etc., λ is put equal to infinity then

$$n = A.$$

The effect in general hould be to de-
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per omson[40], and
Blo th increasing
freq her[43] find that
ther ollock and
Vonw cally the same
no m ond or only 50
per istributed it
is not unlikely that whether there is an increase or not depends upon

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The maximum current to be taken from one of these cells, without injury to cell, is one and one-fourth (1 1/4) amperes.

A. P. Carman

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[38] J. C. Maxwell, Electricity and Magnetism, Vol. 2, Art. 786.

[39] N. Schiller, Pog. Ann., Vol. 152, p. 535, (1874).

[40] J. J. Thomson, Proc. Roy. Soc., Vol. 46, p. 292, (1889).

[41] M. Blondlot, Comptes Rendus, p. 1058, (1891), also Phil. Mag. Series 5, Vol. 32, p. 230, (1891).

[42] E. Cohn and L. Arons, Wied. Ann., Vol. 28, p. 454, (1886), and also Wied. Ann., Vol. 33, p. 13, (1888).

[43] E. Lecher, Wied. Ann., Vol. 42, p. 142, (1891).

[44] J. A. Pollock and O. U. Vonwiller, Phil. Mag. Vol. 3, p. 586, (190

X THE EFFECT OF FREQUENCY ON THE DIELECTRIC CONSTANT

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$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + - - - - - .$$

If after determining the constants A, B, C etc., λ is put equal to infinity then

$$n = A.$$

The effect in general then, of using high frequency should be to decrease the value of k as calculated from the above formula. The experimental evidence is divided. Schiller[39], J. J. Thomson[40], and Blondlot[41] find that for glass there is a decrease with increasing frequency, on the other hand Cohn and Arons[42] and Lecher[43] find that there is an increase while the more recent workers, Pollock and Vonwiller[44] find the dielectric constant to be practically the same no matter whether the frequency is 20 million per second or only 50 per second. Since the values for glass is so evenly distributed it is not unlikely that whether there is an increase or not depends upon

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[38] J. C. Maxwell, Electricity and Magnetism, Vol. 2, Art. 786.

[39] N. Schiller, Pog. Ann., Vol. 152, p. 535, (1874).

[40] J. J. Thomson, Proc. Roy. Soc., Vol. 46, p. 292, (1889).

[41] M. Blondlot, Comptes Rendus, p. 1058, (1891), also Phil. Mag. Series 5, Vol. 32, p. 230, (1891).

[42] E. Cohn and L. Arons, Wied. Ann., Vol. 28, p. 454, (1886), and also Wied. Ann., Vol. 33, p. 13, (1888).

[43] E. Lecher, Wied. Ann., Vol. 42, p. 142, (1891).

[44] J. A. Pollock and O. U. Vonwiller, Phil. Mag. Vol.3,p.586,(190

the particular sample used. For most other materials the value of the dielectric constant does decrease with increasing frequency. Numerous examples might be cited but only one rather extreme case will be given; namely, that of Willson[45] who gives the following values for frozen glycerine.

Temperature	Frequency	Dielectric Constant
-44°C	100	54.
-48°C	2000000	3.97

The change in the case of highly purified selenium and kerosene is very small if it exists at all. Vonwiller and Mason[46] have investigated the former with the following results.

Temperature	Frequency	Dielectric Constant
16°C	50	6.13
23.6°C	24000000	6.14

while Anderson[47] working at the University of Illinois was able to find no change in the latter for the range for frequencies lying between 1 and 1600000.

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[45] E. Willson, Proc. Roy. Soc., Vol. 71, p. 241. (1903).

[46] O. U. Vonwiller and W. H. Mason, Proc. Roy. Soc., Series A, Vol. 79, p. 175, (1907).

[47] S. H. Anderson, Phys. Rev., Vol. 34, p. 34, (1912).

XI WORK DONE ON ICE AND WATER

Many investigators have studied the dielectric constant of water at temperatures above 0°C. Thwing[48] has found a very decided maximum at 4°C i.e., the point of greatest density. Later investigators[49] have not been able to find such a maximum but all are agreed that there is a marked decrease with the temperature. The value given for 0°C, while varying somewhat according to the method used is generally around 85. It is approximately the same whether determined by a high speed or by a low speed method, also Maxwell's law is found to hold at least with a fair degree of approximation. An exception* to this is value obtained by Beaulard[50] who has done considerable work on water. His method consists in measuring the torque exerted on a glass or quartz ellipsoid filled with the dielectric substance and placed unsymmetrically in a rapidly alternating electrostatic field. He gives values ranging from 11. to 3 for water at the freezing temperature. The higher values are thought to be incorrent due to the solution of glass by the water. Palmer[51] has carried on some work in regard to the change of the temperature coefficient with frequency,

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[48] C. B. Thwing, Phys. Rev., Vol. 2, p. 35, (1894-5) or Zeit. f. Phys. Chem., Vol. 14, p. 286, (1894).

[49] L. Drude, Wied, Ann., Vol. 59, p. 17, (1896).
F. Heerwagen, Wied. Ann., Vol. 49, p. 278, (1893).
O. U. Vonwiller, Phil. Mag., Series 6, Vol. 7, p. 655, (1904).

*See also R. A. Fessenden, Phil. Mag., Vol. 38, p. 567, (1894). and reply to same by J. Hopkinson, Phil. Mag., Vol. 39, p. 134, (1895).

[50] F. Beaulard, Rev.Electrique, Vol. 4, p. 119, (1905).
Comptes Rendus, Vol. 141, p. 656, (1905).
Jour. de physique, Vol. 5, p. 165, (1906).
Comptes Rendus, Vol. 144, p. 904, (1907), or Electrician, Vol. 59, p. 393, (1907).
Comptes Rendus, Vol. 146, p. 960, (1908).

[51] A. de Forest Palmer Jr., Phys. Rev., Vol. 16, p. 267, (1903).

which seems to give interesting results. The equation $k_t = k_{17}(1 + b_{17}(t - 17))$ is used to express the relation between the dielectric constant at temperature t with the value at 17°C, b_{17} being the temperature coefficient calculated from 17° and a negative quantity. Although the evidence is insufficient, his values of b_{17} when compared with other values obtained by various authors using various frequencies makes it very probable that b_{17} is dependent upon the frequency, that it increases to a maximum and then decreases to its original value as the frequency varies from 100 to 100000000 per second.

In the case of ice the effect of frequency is very marked. Hopkinson[52] has shown that with electromotive force reversals of the order of 10 to 100 per second the dielectric constant - at some temperature presumably not far removed from zero is around 80, while with reversals such as 1000000 per second the number falls to less than 3. This important observation brings into accordance the apparently conflicting high values of Bouty[53] and Thomas[54] on the one hand with the low ones of Blondlot[55], Perot[56], Thwing[57] and Abegg[58] on the other.

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[52] See note to paper by J. A. Fleming and J. Dewar, Proc. Roy. Soc., Vol. 61, (1897), bottom of page 5.

[53] M. E. Bouty, Jour. de physique, Series 3, Vol.1, p.454, (1892)

[54] P. Thomas, Phys. Rev., Vol. 31, p. 278, (1910).

[55] R. Blondlot, Comptes Rendus, Vol. 119, p. 595, (1894).

[56] A. Perot, Comptes Rendus, Vol. 119, p. 601, (1894).

[57] C. B. Thwing, loc. cit.

[58] R. Abegg, Wied. Ann., Vol. 65, p. 229, (1898).

At low temperatures the work is interesting. Abegg[59] has published the following data for temperatures as low as -80°C.

Temperature	Dielectric Constant	
(+10.0°C	83.8	Determination by Ratz)
-20.0	101.	
-40.	112.	
-60.	127.	
-80.	137.	

In some previous work on liquids he derived the formula $k_t = Ce^{-\frac{T}{190}}$, T being the absolute temperature and C the dielectric constant at absolute zero. The formula holds well for the various liquids investigated and gives fair agreement for the values quoted above. The value of C to be used in the case of ice is 372 and hence this was the value prophesied for the dielectric capacity of ice at absolute zero. The later work of Thomas[60] confirms the values given by Abegg. He gives:

Temperature	Dielectric Constant
-2°C	93.9
-3	94.3
-5	93.6
-9	95.3
-12	95.6
-15	96.0
-18	96.4

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[59] R. Abegg, Wied. Ann., Vol. 60, p. 54, (1897).

[60] P. Thomas, loc. cit.

which shows conclusively that there is an increase in the constant as the temperature decreases. Fleming and Dewar[61] working at liquid air temperatures and with a slow speed method did not bear out Abegg's prediction. They find a value of about 3 at these temperatures, a number which has been checked by Thomas[62]*. Behn and Kiebitz[63] have found that with a high speed method the value is $n_\infty^2 = (1.32)^2 = 1.74$ a number which does not vary markedly from the value obtained by similar methods for the higher temperatures.

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[61] J. A. Fleming and J. Dewar, Proc. Roy. Soc., Vol. 61, p. 316, (1897).

[62] P. Thomas, loc. cit.

* Under the discussion of results Thomas states that the dielectric constant of liquid air was found to be 3.0, but an inspection of Table VIII in his paper and the note preceding it, indicate that this is an error and that the dielectric constant of ice at liquid air temperature was meant instead.

[63] U. Behn and F. Kiebitz, Boltzmann Festschrift, p. 610, (1904).

XII THE DIELECTRIC CONSTANT AND TEMPERATURE

Various authors have studied the variation of the dielectric constant with temperature but they have, as a rule, been interested only in determining the temperature coefficient. This should, if we accept the Clausius-Mosotti relation be a negative quantity as can be shown by the following reasoning.

We have given

$$\frac{k - 1}{(k + 2)d} = C .$$

The density from definition is equal to $\frac{m}{v}$. Now the coefficient of cubical expansion for every known substance, except silver iodide, is a positive quantity and hence the density at any temperature is $\frac{m}{v(1+bt)}$. If we insert this in the relation we get

$$\frac{k - 1}{\frac{(k+2)m}{v(1+bt)}} = C$$

or

$$\frac{k - 1}{k + 2} = \frac{mc}{v(1+bt)} = \frac{C_1}{(1+bt)} .$$

With increasing temperature the right hand member will become smaller and hence the left hand member must also. This can only happen, as k is positive and greater than unity, if k decreases. The experimental evidence shows that there may be either an increase or a decrease. Cassie[64], one of the first workers in this field, made several determinations between the temperature range 11° to 60°C. Mica, ebonite, glass and paraffin oil showed an increase while turpentine, carbon disulphide, glycerine, benzoline, benzine and olive oil showed a decrease. Pellat and Sacerdote[65] verified the work in

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[64] W. Cassie, Proc. Roy. Soc., Vol. 46, p. 357, (1889).

[65] H. Pellat and P. Sacerdote, Comptes Rendus, Vol.127,p.544(1898)

regard to ebonite and have added paraffin to the list of those that decrease with temperature. Analagous results have been obtained by Curie and Compan[66] who find that at -75°C ebonite, mica, quartz and glass still have a positive coefficient. For water at 17° Coolidge[67] has given -0.432, a value which agrees well with that obtained by Drude and Heerwagen. More recent work than this has been done by Niven[68] from whom the following values are taken.

Temperature	Dielectric Constant	Temperature Coefficient
0°C	90.36	——
7	80.06	——
33	69.31	-0.64
59.5	58.32	-0.54
83	37.97	-0.63

Fleming and Dewar[69] who have done considerable work at low temperatures find, that for a very large number of organic compounds and frozen electrolytes there is a very large increase as the temperature is increased. The meaning of this temperature coefficient has been subject to some mathematical treatment. These papers will not be discussed here but if the reader is interested he may consult the following.

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[66] J. Curie and P. Compan, Comptes Rendus, Vol.134,p. 1295, (1902).

[67] W. D. Coolidge, Wied. Ann., Vol. 69, p. 125, (1899).

[68] C. Niven, Proc. Roy. Soc., Series A., p 139, (1911).

[69] J. A. Fleming and J. Dewar, Various papers in Vol. 61, (1897) of the Proceedings of the Royal Society.

Foster and Porter's Elementary Treatise on Electricity and Magnetism, 3d Edition, p. 95.

J. Koenigsberger, Ann. d. Physik, Series 4, Vol. 5, p. 113 (1901).

J. Kroò, Phys. Zeit., Vol. 13, p. 246, (1912)

P. Debye, Phys. Zeit., Vol. 13, p. 97, (1912).

XIII OTHER OBSERVATIONS ON THE DIELECTRIC CONSTANT

A principle known as the Nernst-Thomson rule has been stated which expresses the relation between the dielectric constant and the dissociating power of a solvent. It is:-

The greater the dielectric capacity of a solvent, the greater will be the degree of dissociation of a substance dissolved in it, other conditions being the same.

This rule only expresses a rough parallelism, Although well substantiated by the work of Walden[70] on over fifty different solvents still Schlundt[71] and Kahlenberg[72] have published quite a number of exceptions. Other rules having only a general application have been found. As the values of the dielectric constant decreases the values of the latent heat of vaporization and of the critical pressure decrease while the values of "a", Van der Waal's constant increases. The effect of a magnetic field upon capacity has been tried without result. Roberts[73] has measured the capacity of a condenser when placed in a field of 1500 lines/sq. cm. The method used was an accurate one giving results which checked within .07%. He could detect no change.

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[70] P. Walden, Zeit. f. Phys. Chem., Vol. 54, p. 129, (1906).

[71] H. Schlundt, Journ. Phys. Chem., Vol. 5, p. 157and503,(1901).

[72] L. Kahlenberg, Zeit. f. Phys. Chem., Vol. 23, p. 309, (1903).

[73] E. C. Roberts, Phys. Rev., Vol. 12, p. 50, (1901).

PART II

EXPERIMENTAL

I METHODS TESTED OUT IN THIS INVESTIGATION

Before beginning the investigation proper a number of methods of measuring capacity were tried in order to find the one best adapted to our purpose. The first was the bridge method. Figure 1 shows the connections.

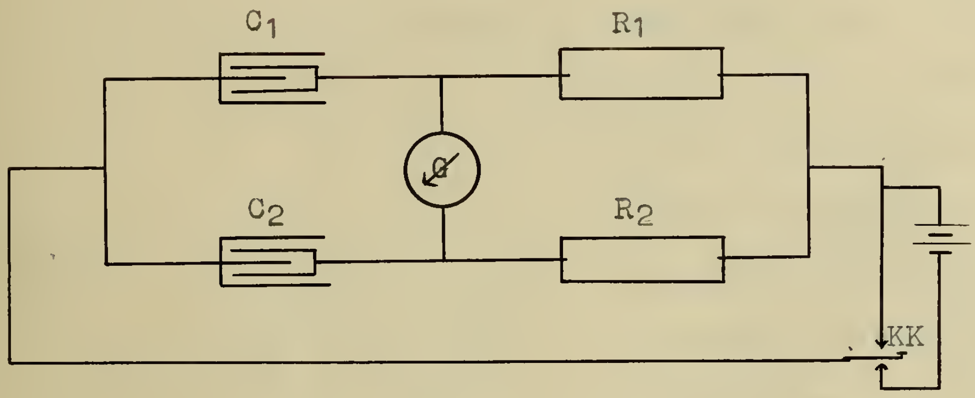

Figure 1

The manipulation consists in changing the values of the resistances, R_1 and R_2 until operating the Kemp key KK causes the galvanometer to show no deflection. When this has been accomplished, the potentials of the points A and B have remained equal during the time of charge. Under these conditions

$$\frac{Q_1}{Q_2} = \frac{C_1}{C_2}$$

and

$$\frac{Q_1}{Q_2} = \frac{R_2}{R_1}$$

whence

$$\frac{C_1}{C_2} = \frac{R_2}{R_1}$$

or

$$C_1 = \frac{C_2 R_2}{R_1}$$

This method was not found suitable as it is not sufficiently sensitive and does not work well for small capacities. This is perhaps due to the capacities of the resistance boxes being too large to be neglected[74]. A method recently published by Campbell[75] was also tried. It is a modification of a scheme devised by Maxwell. The set up is in some respects similar to the preceding one. A rotating commutator R.C. is so arranged as to cause connection to be made at A and B (Fig. 2) simultaneously. The frequency used is such that the condensers are completely charged and discharged during each cycle. When this is done and the resistances R_1 and R_2 adjusted so that there is no galvanometer deflection, then

$$\frac{C_1}{C_2} = \frac{R_2}{R_1}$$

or

$$C_1 = \frac{C_2 R_2}{R_1}$$

the same equation as before. This method proved to be sufficiently accurate but was not used because the capacities of the resistances enter in the same way as they do in the bridge method and because

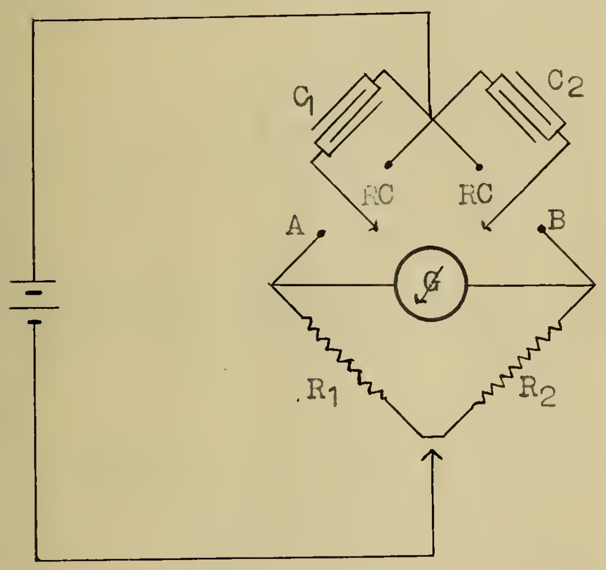

Figure 2

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[74] S. H. Anderson loc. cit.

[75] Albert Campbell, Proc. Phys. Soc. London, Vol. 24, p. 181, (1912).

the balances could not be obtained quickly. Furthermore one could not be certain with the commutator used, that connection was made at A and B simultaneously.

The method finally decided upon was the one known as rapid charge and discharge. Of all schemes of measuring small capacities it is perhaps the most satisfactory if applied to condensers in which there is not much absorption. It consists in rapidly charging and discharging the condenser through a galvanometer, the discharges being sufficiently rapid so as to produce the equivalent of a continuous current. The principle of the method may be illustrated by imagining the prong of the Kemp key, KK, in figure 3 to be caused to vibrate rapidly. The equivalent of this is generally done by means of a sechometer or rotating commutator. For this purpose an instrument made by Edelmann of München was tried. It however proved unsatisfactory as the carbon brushes were found to leave a streak on the quartz plates which insulated the two commutator bars, and thus caused a small leakage. The mechanical construction of the piece was also not good. After various unsuccessful attempts to correct this, the sechometer was discarded and a more satisfactory piece of apparatus made in the physics shop.

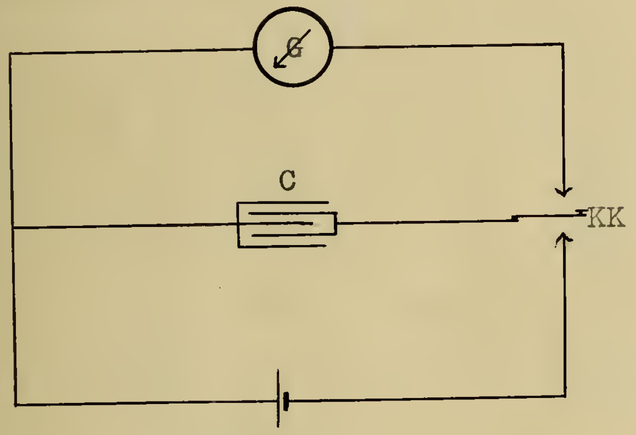


Figure 3

II. DESCRIPTION OF APPARATUS.

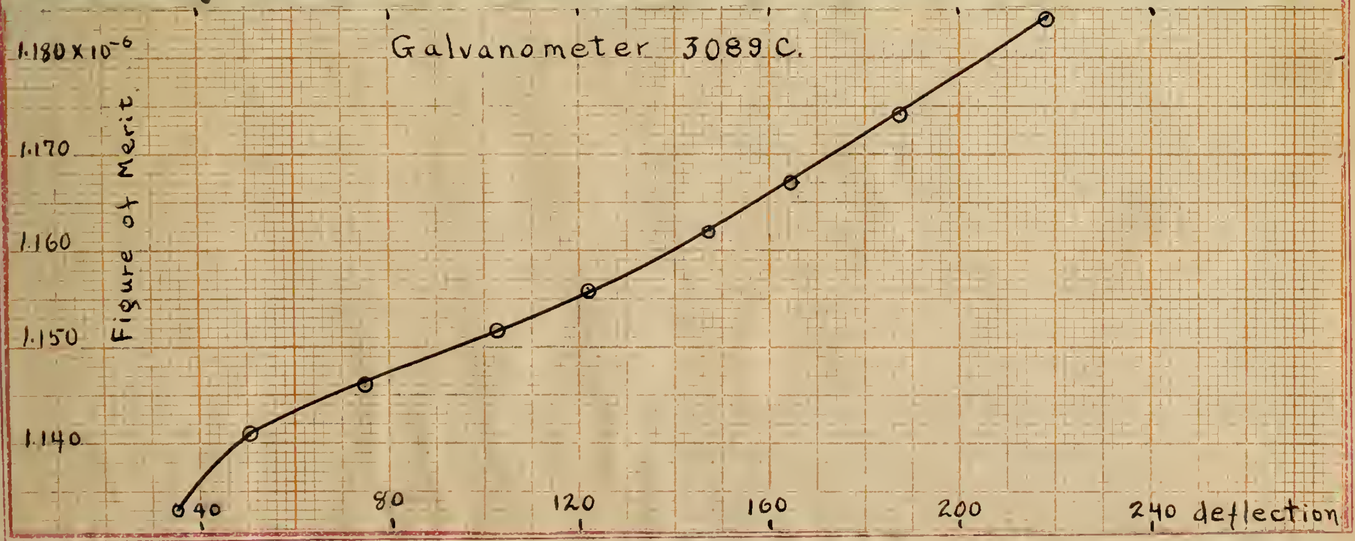
Resistances.- Three resistance boxes in all were used (P.L. 3327-A, P. L. 3327-B, P. L. 3329-C). They were standard non-inductance resistance taken from the general stock of apparatus reserved for research use. The boxes were made by Otto Wolff and were accurate to one fifteeth of one percent.

Galvanometers.- Two D'Arsonval galvanometers (P.L. 3089 K. and P. L. 3089 C., both "Type H" instruments as made by Leed, Northrup & Co.) were used. 3089 K was made ballistic and placed in the discharge circuit from the condenser. This instrument, although sufficiently sensitive when used with the telescope and curved scale provided, had to be read by means of a telescope and scale placed about 1.2 meters away in order not to interfere with the set up. Its constants were: Resistance approximately 1100 ohms

Figure of merit, scale at 1.2 m. distance approximately .3 x 10^{-8} amp./mm.

Undamped period 6.77 seconds.

3089 C was used in the thermo-couple circuit. Its constants were accurately determined. They were: Resistance at 23°C 254.7 ohms



*Average figure of merit
1.157×10^{-8} amp./ mm.

Thermocouple.- The thermocouple was composed of iron-constantan. The individual wires were 0.23 mm. in diameter, having been drawn down from larger sizes and then annealed so as to render them more flexible. During an experiment the warm junction of the element was placed in a Dewar cylinder filled with water which had assumed room temperature. In series with the couple and the galvanometer was a constant resistance (P. L. 3327 A) of 1800 ohms which served to cut down the deflection so that the maximum reading would still be on the scale.

Such a couple has been previously used by Holborn and Wien[76] for low temperature work. They have compared the element at two temperatures -189.1°C and -78.3°C with the hydrogen thermometer the warm junction being kept at zero. They found the relation between temperature difference and electromotive force expressed in microvolts to be,

$$t = -0.01780\ e - 0.0000008784\ e^2,$$

an equation which indicates that t varies markedly from being a linear function of d. At first it was not thought necessary to calibrate the couple but that the above equation thrown into the following form would be sufficient.

Putting $a = -0.01780$ and $b = -0.0000008784$ we have,

$$t = ae + be^2.$$

If we divide by R^2, that is, the square of the resistance of the

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*Curve shows the variation of the figure of merit with the deflection.

[76] Holborn and W. Wien, Wied. Ann.Vol. 59 , p. 213 (1896)

thermo-couple circuit $(2108.5)^2$ we get

$$\frac{t}{R^2} = \frac{a}{R}\,\frac{e}{R} + b\,\frac{e^2}{R^2}$$

or

$$\frac{t}{R^2} = \frac{a}{R}\,i + b\,i^2,$$

i being the current in micro-amperes. But i = kd, k being the figure of merit and d the galvanometer deflection. Substituting this in the equation it becomes,

$$\frac{t}{R^2} = \frac{a}{R}\,kd + b\,k^2d^2$$

or

$$t = Ra\,kd + b\,R^2k^2d^2.$$

The values of a, b and R were known and the value of k determined for the particular deflection. Hence the relation between t and d were known. However, temperatures calculated by means of this equation were all too low; for instance the computed temperature of liquid air being only -99.9°, a value entirely out of reason. This may be taken to show that the above equation does not hold for all iron-constantan thermo-couples*.

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* There is a bare possibility that the couple was not iron-constantan as no analysis was made to ascertain the exact composition. The average thermo electromotive force per degree was only 25.7 micro-volts whereas it is generally stated as about 50. The wires were taken from spools labeled iron and constantan.

The above fact made calibration an absolute necessity. This was done by using the junction in the condenser as the constant temperature one. As the deflection for liquid air was the same no matter which junction was kept at a constant temperature, it was thought that no appreciable error would enter into the work. For calibration points the following were used; the melting point of ice, the melting point of toluol, the melting point of benzene, the melting point of mercury, the boiling point of liquid oxygen. All of the above materials were the purest that could be obtained. The liquid oxygen was prepared by allowing four day old liquid air to remain in the open air for a number of hours.

The results of the calibration are shown in the following table.-

Calibration of Thermo-element

Temperature of warm junction 27°C.

Temperature of cold junction.	Temperature difference	Galvanometer deflection
-182.5°C	209.5°C	213.0 mm
-102.0	129.0	150.0
- 38.8	65.8	86.2
- 00.0	27.0	37.8
+ 5.5	21.5	29.5

Commutator.- The rotating commutator used in this research was modeled after one described by Fleming and Clinton[77] in their work on the measurement of the capacity and inductance of wireless

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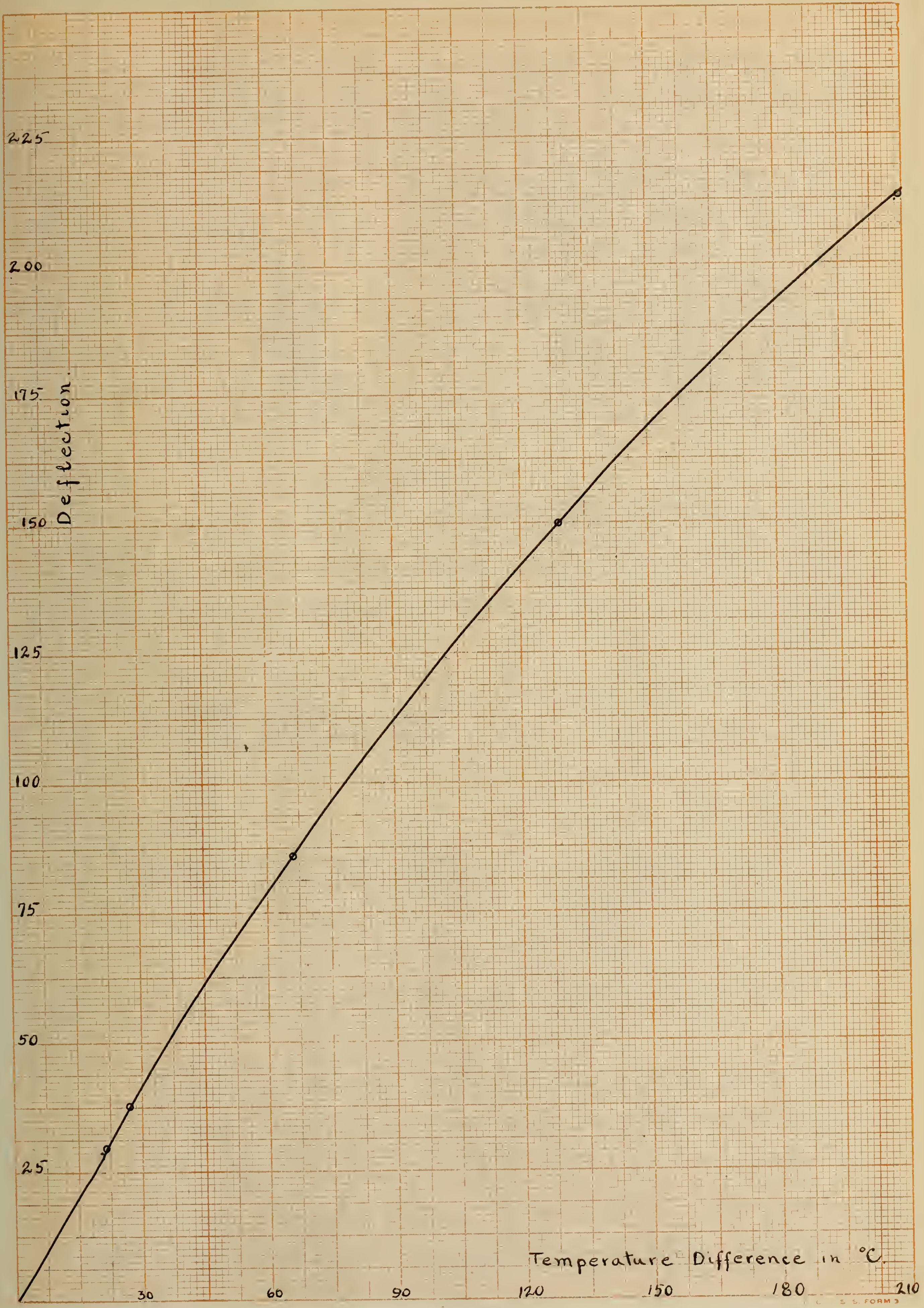
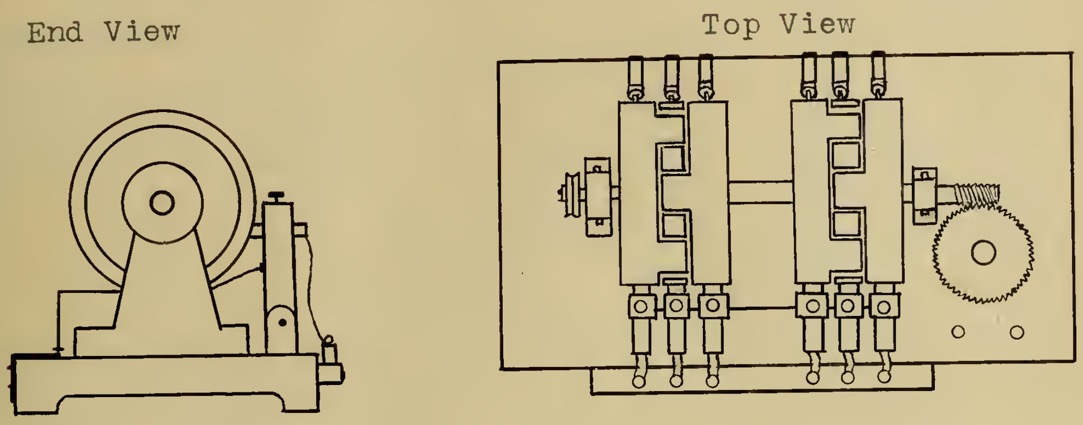
[77] J.A.Fleming and W.C.Clinton, Phil. Mag.(6)Vol.5 p493 (1903)


225
200
175
150
125
100
75
50
25
Deflection.
Temperature Difference in °C.
30
60
90
120
150
180
210

S. S. FORM 3

antenae. It was made double so as to increase its general usefulness. For the present work, however, only one commutator was used.


End View

Top View

Figure 4

Each of the commutators consist essentially of three gun-metal wheels against which three woven wire brushes press. The development of their surfaces is shown in Fig. 4. It is the duty of the middle brush to pass along the path ABC, being connected first with one of the remaining brushes and then with the other. BB are merely rests to carry the brush from A to C. The various parts are insulated by air where ever possible, otherwise by ebonite.

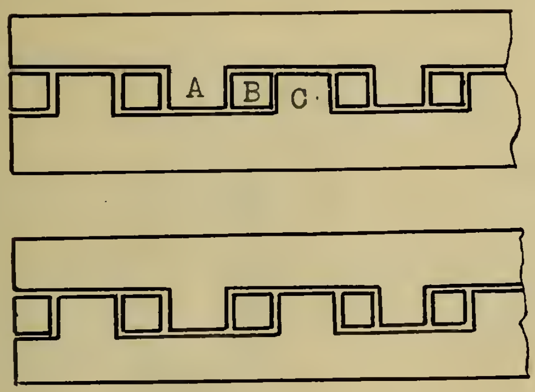


Figure 5

The commutator was belt driven by a one-eighth power Emerson induction motor. This arrangement caused considerable trouble at first due to static charges which were formed by the friction of the belt on the commutator pulley. These influenced the discharge through the galvanometer. The difficulty was finally eliminated

by grounding the commutator shaft.

The number of revolutions were counted by means of a cam wheel attached by a worm gear to the shaft. At every 100 revolutions, a piece of spring brass which pressed against the cam, snapped against a brass peg and made electrical connection with a sounder. Every tap of this sounder then, meant 400 charges and discharges of the condenser, as at every revolution of the commutator the condenser was charged and discharged four times. This instrument was a particularly delightful one to work with, as it required absolutely no attention after the trouble of static charges was eliminated.

Condenser.- A conical condenser of the type used by Fleming and Dewar[78] in their work on frozen electrolytes was found to be the most satisfactory of a number tried. This was made of heavy brass and so designed that any expansion of the frozen water would tend to lift the inner cone and thereby prevent bulging of the sides. It was made as large as the Dewar bulb into which it was to be lowered would permit. The distance between the condenser walls was made small- about 2mm.- in order to increase the capacity. The taper was small so that any lifting of the inner cone would not change the distance between the walls by any appreciable amount. The inner

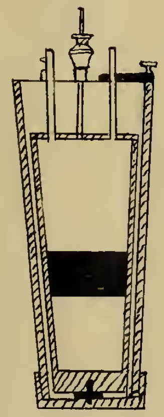


Figure 6

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[78] J.A.Fleming and J. Dewar. Proc. Roy. Soc. Vol. 61 p299 (1897)

cone was centered at the bottom by an ebonite pin and was held in place at the top by means of a three arm carrier made of the same material. This carrier was fastened to the outer cone by three thumb screws and could easily be removed. The thermocouple wires were lead into the inner cone through two metallic tubes at the top and the solder joint was tightly pressed against the wall by an ebonite block turned accurately to fit the taper. Where the wires were in contact with metal, they were protected with a heavy rubber covering.

The top of the inner cone was fastened by six machine screws and a water-tight joint between the two surfaces was insured by placing a thin sheet of lead foil between the two before tightening the screws.

III. PLATINIZING THE CONDENSER.

Attempts made to use the condenser not plated were unsuccessful. Turpentine after remaining in contact with the brass for some time assumed a bright green appearance, while distilled water became turbid. Aside from this the condenser became an electrolytic cell and when short circuited across the galvanometer, deflections were obtained which were entirely off the scale. To overcome these difficulties platinum plating was resorted to. The method used was one recommended by Dr. C. T. Knipp of this laboratory. The formula for the preparation of the bath is to be found in Langbein[79]

It consists of:		
	Platinum chloride	0.245 oz.
	Sodium phosphate	4.94 oz.
	Ammonium phosphate	0.99 oz.
	Sodium chloride	0.245 oz.
	Borax	0.087 oz.

The above is dissolved in six quarts of water and boiled for ten hours, the water lost by evaporation being constantly replaced. Before attempting plating, the object was cleaned carefully by dipping first in dilute hydrochloric acid and then in water after which it was washed with grain alcohol in order to free it from any grease and then rinsed several times in distilled water. When this had been done, the piece was made the cathode and was placed in the plating bath which was in turn placed in a larger bath of water kept near the boiling point. The current used for depositing the platinum was such as to cause a copious evolution of gas at the

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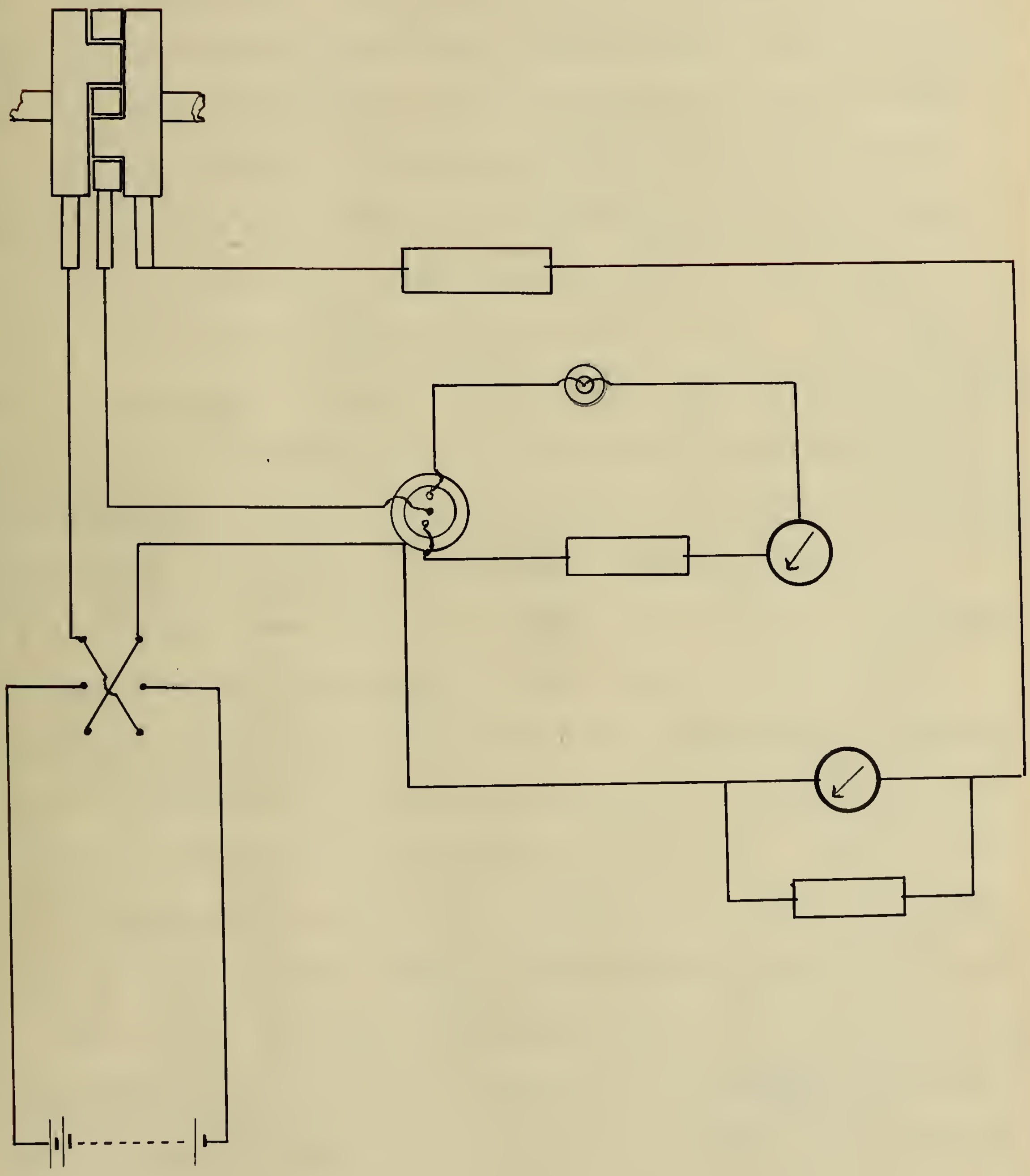
[79] G. Langbein, "Electro-deposition of Metals," translated by W. I. Brannt 3d Edition p. 320.

anode. To accomplish this two group of four gravity cells each, placed in parallel were found to be sufficient. In every case, the anode was a piece of platinum foil arranged so as to be symmetrical with the object. A small hand anode was used to go over the surface of the cathode at a distance of about a quarter of an inch. When the object had remained in the bath about fifteen minutes, it was removed, burnished, cleaned and returned to the bath again for another coat. This operation was repeated several times for each piece.

IV. DIAGRAM OF APPARATUS.



V. MANIPULATION.

Usually before beginning the experiment, the deflection due to the leads and commutator and to the condenser with air as a dielectric were determined. This first deflection was a correction and had to be subtracted from every reading taken during the run.* The next step was to carefully clean the condenser by repeated washings with the water to be experimented upon. It was then placed into position and filled with the sample to a point just a little above the top of the inner cone; next the thermocouple circuit was broken and the galvanometer set on zero. The warm junction of the couple was now placed in the Dewar cylinder containing water at room temperature and the top of the cylinder closed with a cork stopper. With this arrangement the temperature did not change more than a few tenths during the entire experiment.

It was thought best that the sample,which was in every case obtained from the still belonging to the Physics Department- should be frozen gradually. To do this the condenser was emersed about three-fourths way in a bath of denatured alcohol which had been previously cooled to a few degrees below zero. After remaining here fifteen minutes, the water assumed the frozen state and the denatured alcohol was removed. The condenser was next lowered slowly into a Dewar cylinder containing liquid air. After the air had become quiescent and the thermocouple galvanometer had indicated that a constant temperature had been reached, the condenser

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* Or some definite fraction of it if the value of the charging E.M.F. or shunt across the galvanometer had been changed.

was entirely submerged in the liquid air and allowed to remain there a few minutes.

The charging E. M. F. was then read by a voltmeter reading directly to tenths of a volt. The condenser could now be removed from the liquid air and allowed to heat up slowly, observations being made at various intervals on the deflections of both of the galvanometers and the time. Every now and then throughout the experiment a resistance usually about 5000 ohms was placed in the discharge circuit and if a change in the deflection was noted it was taken as an indication that the dielectric had become conducting. Since the deflection depends directly upon the speed of the commutator, the time for 4000 commutations or 1000 revolutions was noted at frequent intervals.

VI EXPLANATION OF EXPERIMENTAL DATA AND CURVES

In the following tables of experimental data, the voltage given refers to the charging e.m.f. of the condenser, and the shunt resistance to the value of the shunt around the galvanometer in the discharge circuit. The readings included in parentheses are zero readings. The frequency is recorded in revolutions of the commutator and must be multiplied by four in order to get the number of charges and discharges in the time given. The time of taking observations is recorded and this with the deflection of the thermo-couple galvanometer give the necessary data for the heating curve. This curve was thought valuable as it indicated the duration of the experiment and when compared with the dielectric constant - temperature curve gave information as to the rate with which the dielectric constant was changing with temperature.

The dielectric constant-temperature curves are plotted as dielectric constant against deflection of the thermo-couple galvanometer and the temperature at intervals of 20° determined by reference to the calibration curve of the thermoelement.

A word might be said in regard to the calibration curve. It should be remembered in using this curve that the ordinates represent temperature differences and not actual temperatures. In order to find the temperature for any deflection, the temperature of the warm junction must be subtracted from the temperature difference as indicated by the curve.

The calculations of the dielectric constants were performed as follows:

If d_c is the deflection due to the leads and commutator and d_a

the deflection due to the air condenser where V_1 is the voltage used and S_1 the galvanometer shunt, and d_i is the deflection due to the ice condenser under the same conditions then,

$$k = \frac{d_i - d_c}{d_a}$$

If however, the voltage has been changed to some value V_2 before determining d_i the expression becomes,

$$k = \frac{\frac{V_1 d_i}{V_2} - d_c}{d_a}$$

Further if both the shunt value and voltage have been changed and the deflection of the air condenser under voltage V_1 and shunt S_2 is given as d'_a then,

$$k = \frac{\frac{d_a}{d'_a} \frac{V_1}{V_2} d_i - d_c}{d_a}$$

In the calculations no attempt was made to correct for changes in frequency. The values are only given to show that there was no great variation in this factor.

VII EXPERIMENTAL DATA AND CURVES

Sample No. 1

Charging voltage 20.7 Warm junction of thermo-couple 23°C

Galvanometer shunt 20 ohms

Reading due to air condenser, leads and commutator	22.18
Zero reading	21.60
Deflection	.58
Reading due to leads and commutator	21.86
Zero reading	21.60
Deflection	.26

Deflection due to air condenser = .58 - .26 = .32

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
The condenser in liquid air			
22.70 (21.60)	2.62	205.5	10:00A.M.
The liquid air removed and the condenser allowed to stand unprotected in the open air.			
22.81 (21.41)	3.60	180.7	10:04
23.50 (21.41)	5.72	173.5	10:08
25.70 (21.41)	12.56	162.0	10:12

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
32.50 (21.42)	33.81	148.0	10:16A.M.

A canton flannel cloth was wrapped around the condenser

38.00 (21.42)	51.00	141.0	10:19

Frequency: 1000 revulutions of commutator per 35 sec.

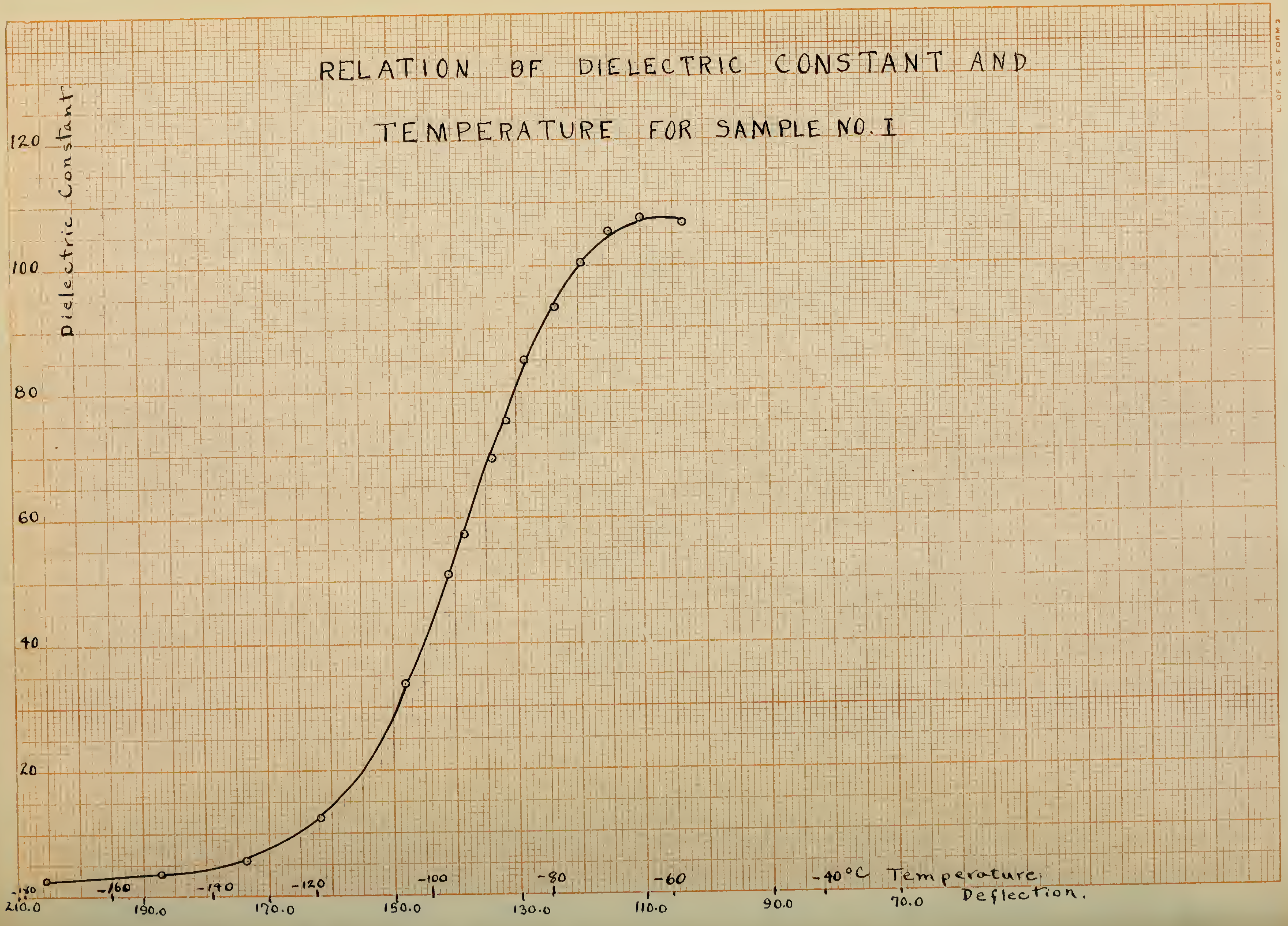
40.00 (21.42)	57.25	138.5	

Voltage changed to 10.37

32.60 (21.42)	69.06	134.3	10:23
33.70 (21.42)	75.94	131.9	10:25
35.20 (21.43)	85.22	128.5	10:28
36.70 (21.43)	94.62	123.6	10:32
37.72 (21.46)	100.81	119.8	10:35
38.40 (21.46)	105.06	115.2	10:41
38.75 (21.46)	107.25	110.0	10:45

Voltage changed to 6.23

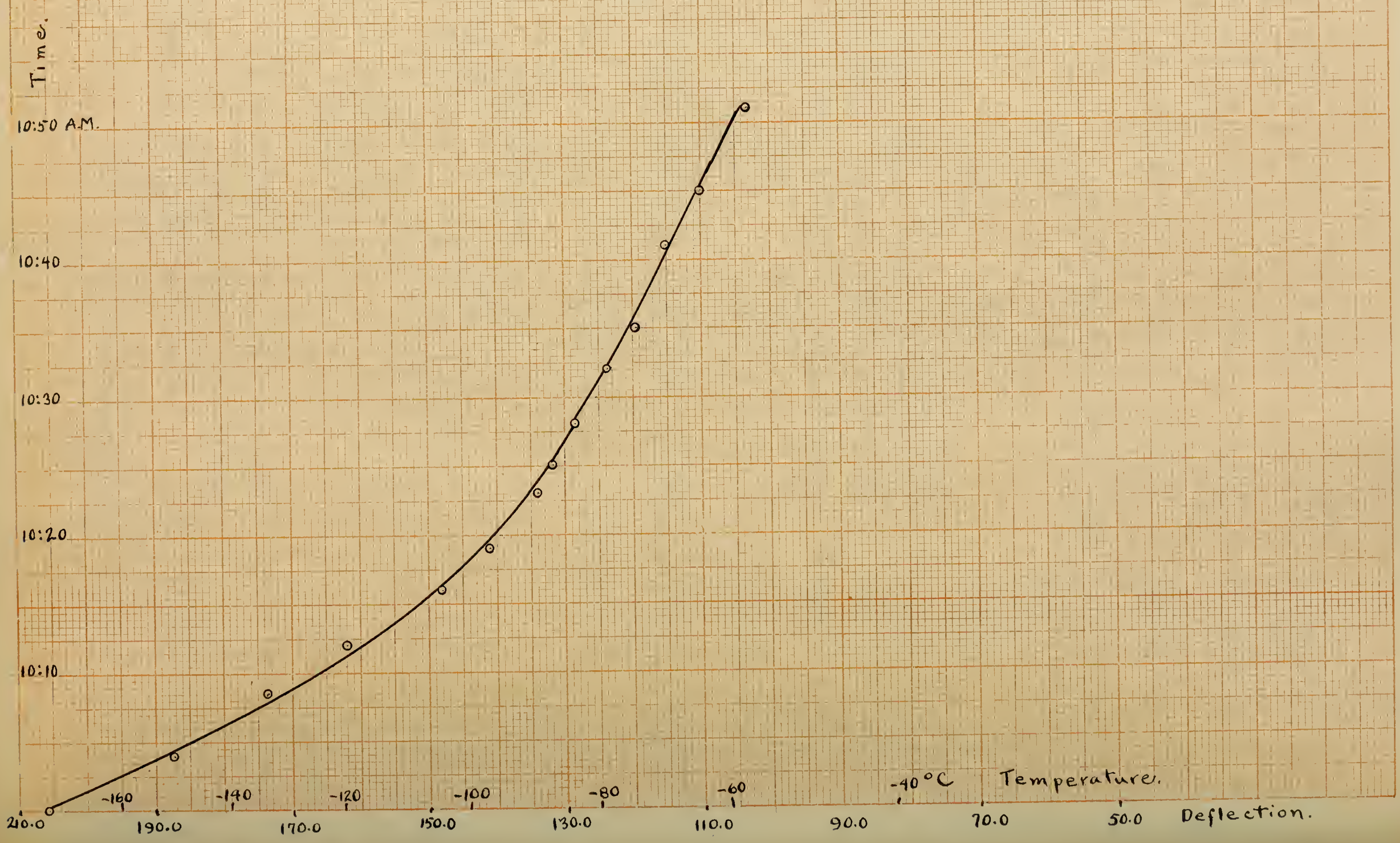
31.83 (21.48)	106.56	103.5	10:51



RELATION OF DIELECTRIC CONSTANT AND TEMPERATURE FOR SAMPLE NO. I

U. OF I. S. S. FORM 3

HEATING CURVE FOR SAMPLE NO. I



U OF . S. S. FORM 3

Sample No. 2

Charging voltage 20.64 Warm junction of thermo-couple 20.5°C

Galvanometer shunt 20 ohms

Reading due to air condenser, leads and commutator		23.58
Zero reading		23.00
	Deflection	.58
Reading due to leads and commutator		23.26
Zero reading		23.00
	Deflection	.26

Deflection due to air condenser = .58 - .26 = .32

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
24.12 (23.00)	2.69	209.2	3.47P.M.

The condenser was transferred to a large Dewar cylinder which had a small hole in the bottom plugged up with cotton waste. The waste was also highly packed in the mouth of the flask.

24.22 (23.00)	3.00	201.5	3:56
24.28 (23.00)	3.44	185.5	4:02

Frequency: 1000 revolutions per 35 sec.

24.35 (23.00)	3.40	179.0	
24.49 (23.00)	3.84	173.0	4:09
24.67 (23.00)	4.40	167.2	4:12

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
25.06 (23.00)	5.63	160.5	4:17P.M.
25.48 (23.00)	6.93	157.0	4:20
25.90 (23.00)	8.25	154.2	4:21
26.70 (23.00)	10.75	151.2	4:23

5000 ohms placed in the discharge circuit does not change the galvanometer reading.

27.90 (23.00)	14.50	148.3	4:26
29.00 (23.00)	17.94	146.0	4:27
30.90 (23.00)	23.87	143.2	4:30
33.00 (23.00)	30.44	140.4	4:32
35.40 (23.00)	37.94	138.0	4:35
38.70 (23.00)	48.25	135.1	4:37
42.00 (23.00)	58.56	132.6	4:39

Voltage changed to 10.33

34.60 (23.00)	71.68	129.0	4:42

Frequency: 1000 revolutions per 35 seconds.

36.20 (23.00)	81.68	126.5	4:45

5000 ohms changes reading to 35.9

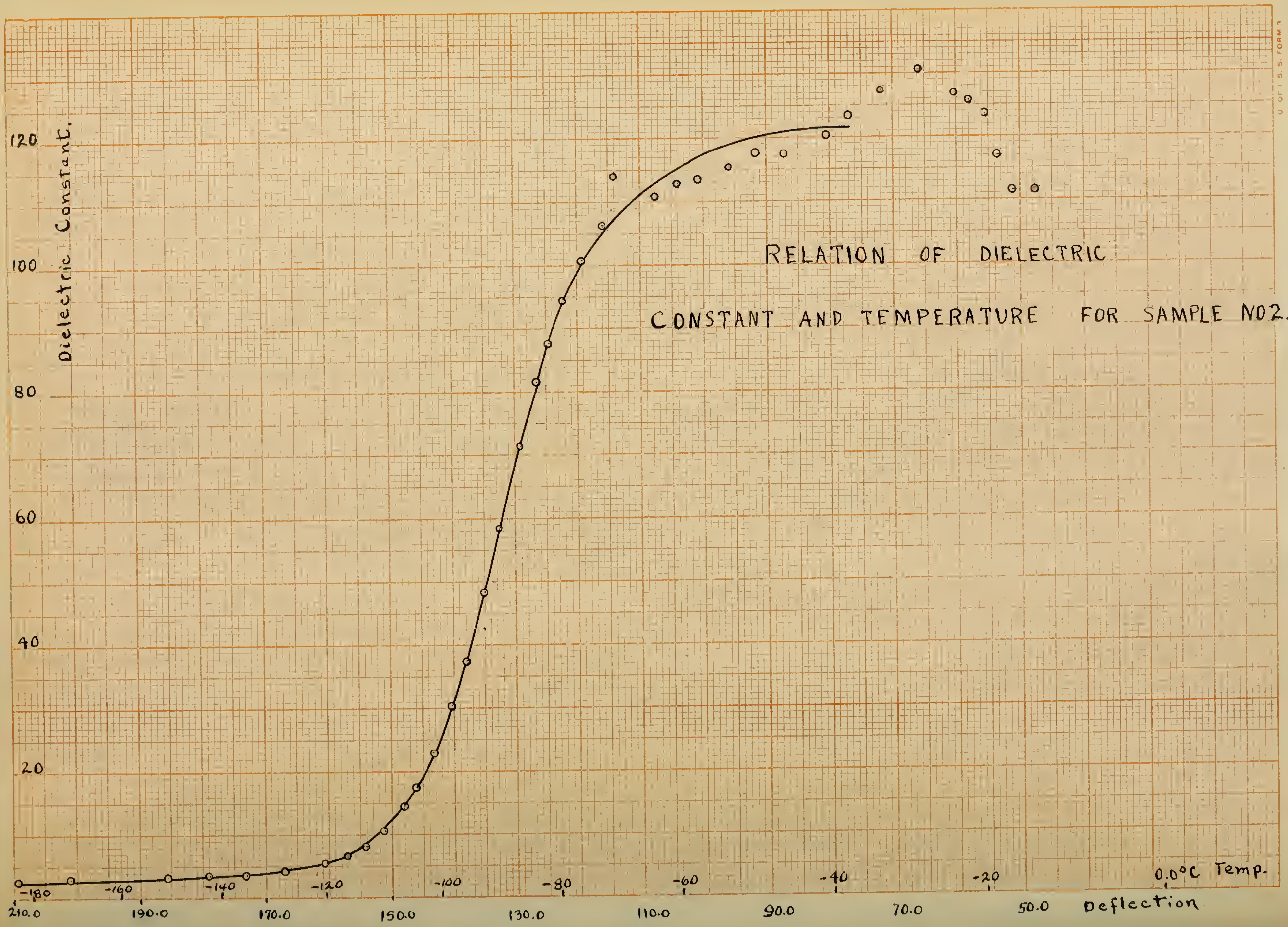
37.20 (23.00)	87.94	124.3	4.46

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
38.30 (23.00)	94.81	122.0	4:49A.M.
39.25 (23.00)	100.75	119.1	4:51
40.00 (23.00)	105.44	116.0	4.54
41.50 (23.00)	114.81	114.3	4.57
5000 ohms changes reading to 40.9			
40.85 (23.00)	110.75	107.9	5:04
Rearranged the waste around the condenser			
41.20 (23.00)	112.94	104.3	5:08
41.33 (23.00)	113.75	100.8	5:12
41.65 (23.00)	115.75	95.2	5:18
41.52 (23.00) Motor Unsteady	118.06	91.9	5:23
42.00 (23.00)	117.93	87.0	
5000 ohms changes deflection to 41.65			
42.45 (23.00)	120.75	80.4	5:40
Voltage changed to 6.21			
35.12 (23.00)	124.94	77.2	5:44
35.20 (23.00)	125.75	76.0	5:46
35.41 (23.00)	127.94	71.8	5:52

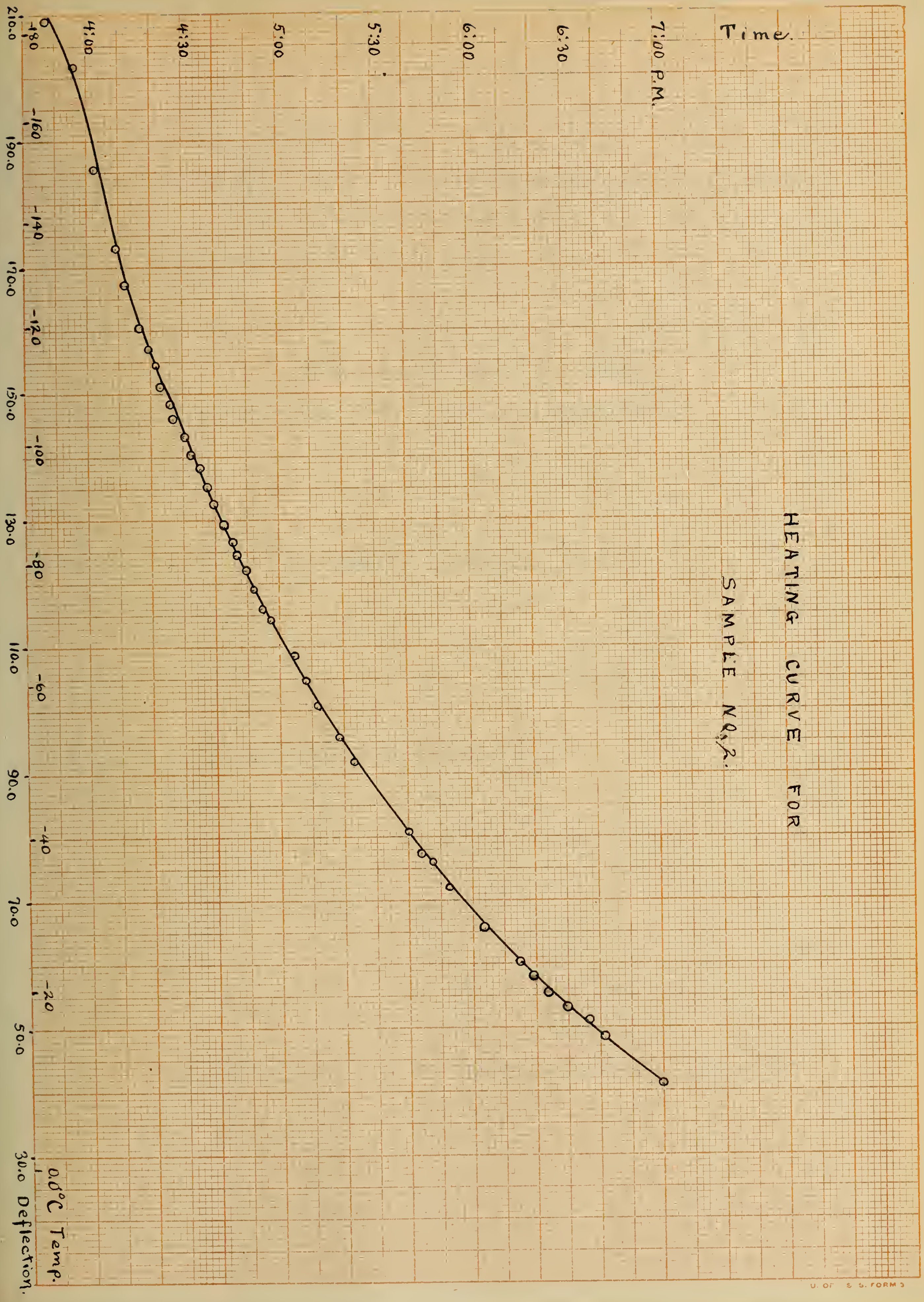
Frequency: 1000 revolutions per 35 seconds

Deflections very unsteady!

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
35.65 (23.00)	130.44	65.8	6:04P.M.
35.30 (23.00)	126.81	60.0	6:15
35.20 (23.00)	125.75	58.0	6:19
5000 ohms changes deflection to 34.80			
34.95 (23.00)	123.15	55.8	6:24
34.36 (23.00)	117.06	53.5	6.29
33.82 (23.00)	111.44	51.0	6:36
32.90 (23.00)	112.28	47.7	6:41
38.00 (23.00)	154.81	40.8	7:00



RELATION OF DIELECTRIC CONSTANT AND TEMPERATURE FOR SAMPLE NO2.


HEATING CURVE FOR SAMPLE NO. 2.

Sample No. 3

A reversing switch was put in the charging current to eliminate any possible thermal e.m.f. in the condenser circuit. When the current is direct, the galvanometer reading will not be preceded by a letter, when reversed the reading will be preceded by an "R".

Charging voltage 20.62 Warm junction of thermo-couple 23°C

Galvanometer shunt 20 ohms

Reading due to air condenser, leads and commutator		23.58	
Zero reading		23.00	
	Deflection	.58	
Reading due to air condenser, leads and commutator		R22.42	
Zero reading		23.00	
	Deflection	.58	
	Average		.58
Deflection due to leads and commutator		23.26	
Zero reading		23.00	
	Deflection	.26	
Deflection due to leads and commutator		R22.74	
Zero reading		23.00	
	Deflection	.26	
	Average		.26

Deflection due to air condenser = .58 - .26 = .32

The condenser removed from the liquid air and packed in the broken Dewar cylinder.

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
24.26 (23.00)	3.13	202.1	4:44P.M.
R21.74 (23.00)	3.31	196.0	4:55
R21.78 (23.00)	3.75	186.0	4:58
24.53 (23.00) R21.32 (23.00)	4.06	179.2	5:03
25.00 (23.00) R20.98 (23.00)	5.47	174.8	5:06
R20.20 (23.00)	7.94	168.5	5:09
26.70 (23.00)	10.75	164.0	5:12
27.70 (23.00)	13.88	161.0	5:15
29.00 (23.00)	17.94	157.8	5:17
30.50 (23.00)	22.62	154.5	5:19
32.50 (23.00)	28.87	151.0	5:22

Voltage changed to 10.31

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
33.00 (23.00)	61.69	138.0	5:32P.M.
39.00 (23.40)	96.69	117.2	5:52

Zero adjusted to 23.00

Frequency: 1000 revolutions per 35 seconds

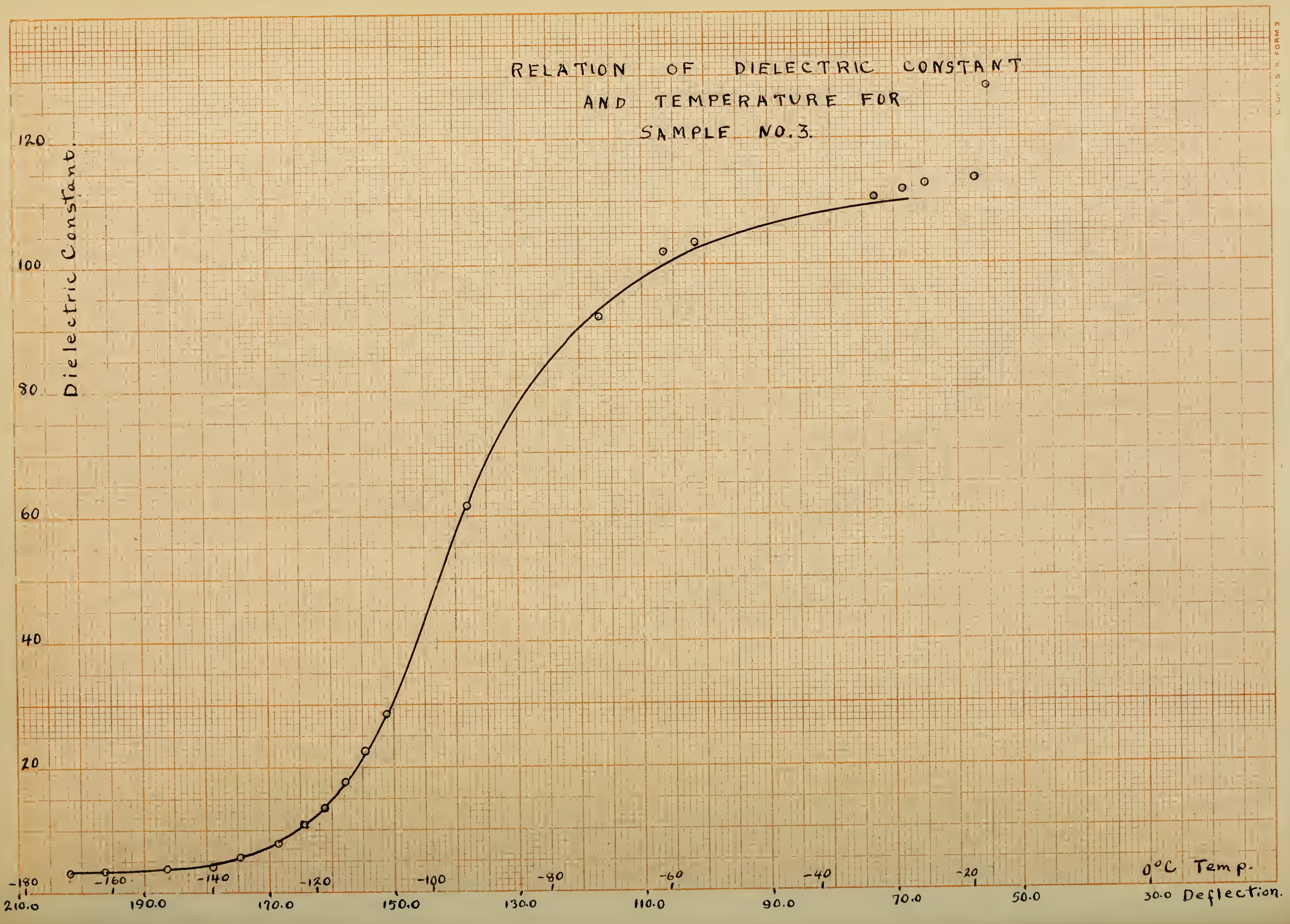
Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
32.92 (23.00) R13.02 (23.00)	102.09	106.8	6:04
33.05 (23.00)	103.47	101.2	6:10

5000 ohms changes deflection to 32.98

Deflections are constant!

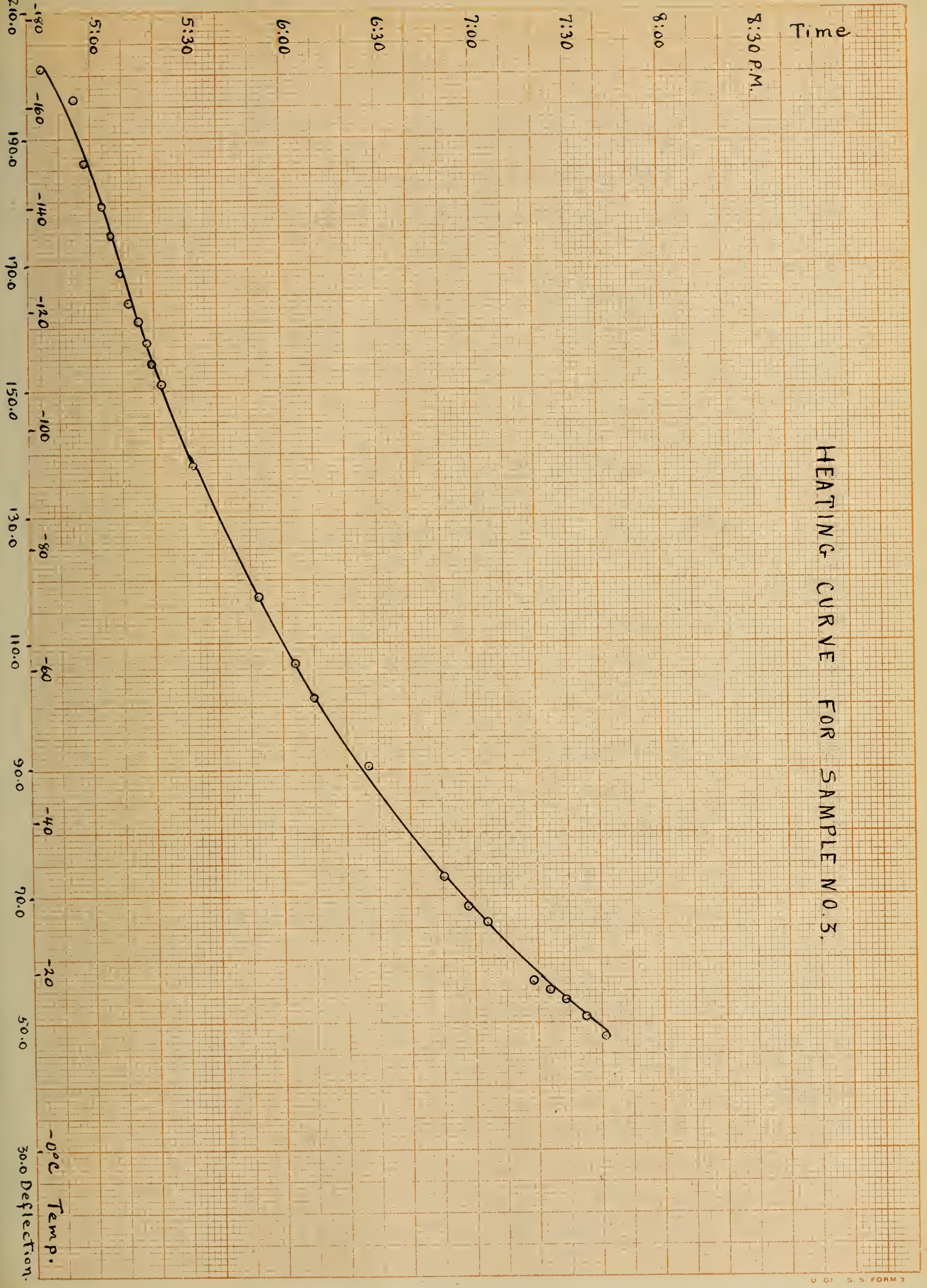
Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
33.75 (23.00) R12.25 (23.00)	110.72	73.0	6:50
34.00 (23.20)	111.25	68.2	6:58
34.19 (23.29)	112.28	65.6	7:04
34.42 (23.29	113.41	56.8	7:19
35:70 (23.29)	127.94	55.2	7:24

The galvanometer acting so erratic that the experiment had to be stopped.



RELATION OF DIELECTRIC CONSTANT AND TEMPERATURE FOR SAMPLE NO. 3.

U OF I S K FORM 3


HEATING CURVE FOR SAMPLE NO. 3.

U OF S. S. FORM 3

Sample No. 4

Charging Voltage 20.62 Warm junction of thermo-couple 24°C

Galvanometer shunt 20 ohms

Reading due to air condenser, leads and commutator		23.60	
Zero reading		23.00	
	Deflection	.60	
Reading due to air condenser, leads and commutator		R22.41	
Zero reading		23.00	
	Deflection	.59	
	Average		.595
Reading due to leads and commutator		23.29	
Zero reading		23.00	
	Deflection	.29	
Reading due to leads and commutator		R22.72	
Zero reading		23.00	
	Deflection	.28	
	Average		.285

Deflection due to air condenser = .595 - .285 = .31

Galvanometer shunt 50 ohms

Reading due to air condenser leads and commutator		24.42	
Zero reading		23.01	
	Deflection	1.42	
Reading due to air condenser leads and commutator		R21.58	
Zero reading		23.01	
	Deflection	1.42	
	Average		1.42

Reading due to leads and commutators		23.70	
Zero reading		23.01	
	Deflection	.69	
Reading due to leads and commutators		R22.32	
Zero reading		23.00	
	Deflection	.68	
	Average		.685

Deflection due to air condenser 1.42 - .685 = .735

Galvanometer shunt 50 ohms

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
The condenser in liquid air			
25.96 (23.00)	2		
	3.08	207.8	4:15P.M.
R20.08 (23.00)			
The liquid air removed and the condenser packed in the broken Dewar cylinder.			
25.85 (23.00	2.95	194.8	4:26
Frequency: 1000 revolutions per 37 seconds			
26.95 (23.00)	4.45	180.8	4:36
Frequency: 1000 revolutions per 36 seconds			
27.42 (23.00)	5.09	178.2	4:38
28.10 (23.00)	6.01	175.6	4:40
29.50 (23.00)	7.91	172.1	4:43

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
R14.70 (23.00)	11.72	168.0	4:46P.M.
33.00 (23.00)	12.68	165.1	4:48
36.00 (23.00)	16.76	161.2	4:52
37.50 (23.00)	18.80	159.0	4:54
R7.00·? (23.00)	20.84	157.6	4:55
R5.50 (22.90)	22.75	156.0	4:56

There is a slow drift of the zero toward 23.00

Frequency: 1000 revolutions per 37 seconds

44.00 (22.90)	27.78	152.0	5:00

Voltage changed to 10.31

35.50 (23.00)	33.09	148.5	5:04
37.30 (23.00)	37.71	146.0	5:06
39.70 (23.00)	43.16	144.0	5:09
43.00 (23.00)	53.50	139.8	5:13
46.00 (23.00)	61.66	137.2	5:15

Voltage changed to 4.19

33.80 (23.00)	71.37	133.9	5:19
R11.00 (23.00)	79.40	131.2	—

5000 ohms changes deflection to 11.25

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
37.40 (23.00)	95.46	124.0	5:31P.M.
Frequency: 1000 revolutions per 37 seconds			
38.30 (23.00)	101.50	119.0	5:37
5000 ohms changes reading to 38.10			
R7.20 (23.00)	104.84	116.1	5:40
R6.90 (23.00)	106.84	113.4	5:44
R6.80 (23.00)	107.51	109.2	5.50
Voltage changed to 2.1			
30.80 (22.80)	104.64	106.2	5:56
30.90 (22.80)	107.29	102.5	6:00
5000 ohms changes reading to 30.87			
30.97 (22.80)	108.23	98.0	6:07
31.05 (22.80)	109.31	92.8	6:15
Zero adjusted to 23.00			
31.38 (23.00)	111.03	88.8	6:24
31.39 (23.00)	111.17	84.7	6:30
5000 ohms changes deflection to 31.34			
31.51 (23.00)	112.78	80.0	6:39
31.72 (23.00)	115.58	75.4	6:48
32.00 (23.00)	119.32	70.0	7:00

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
32.08 (23.00)	120.39	65.5	7:10P.M.
32.30 (23.00)	123.33	62.0	7:19
R13.70 (23.00			

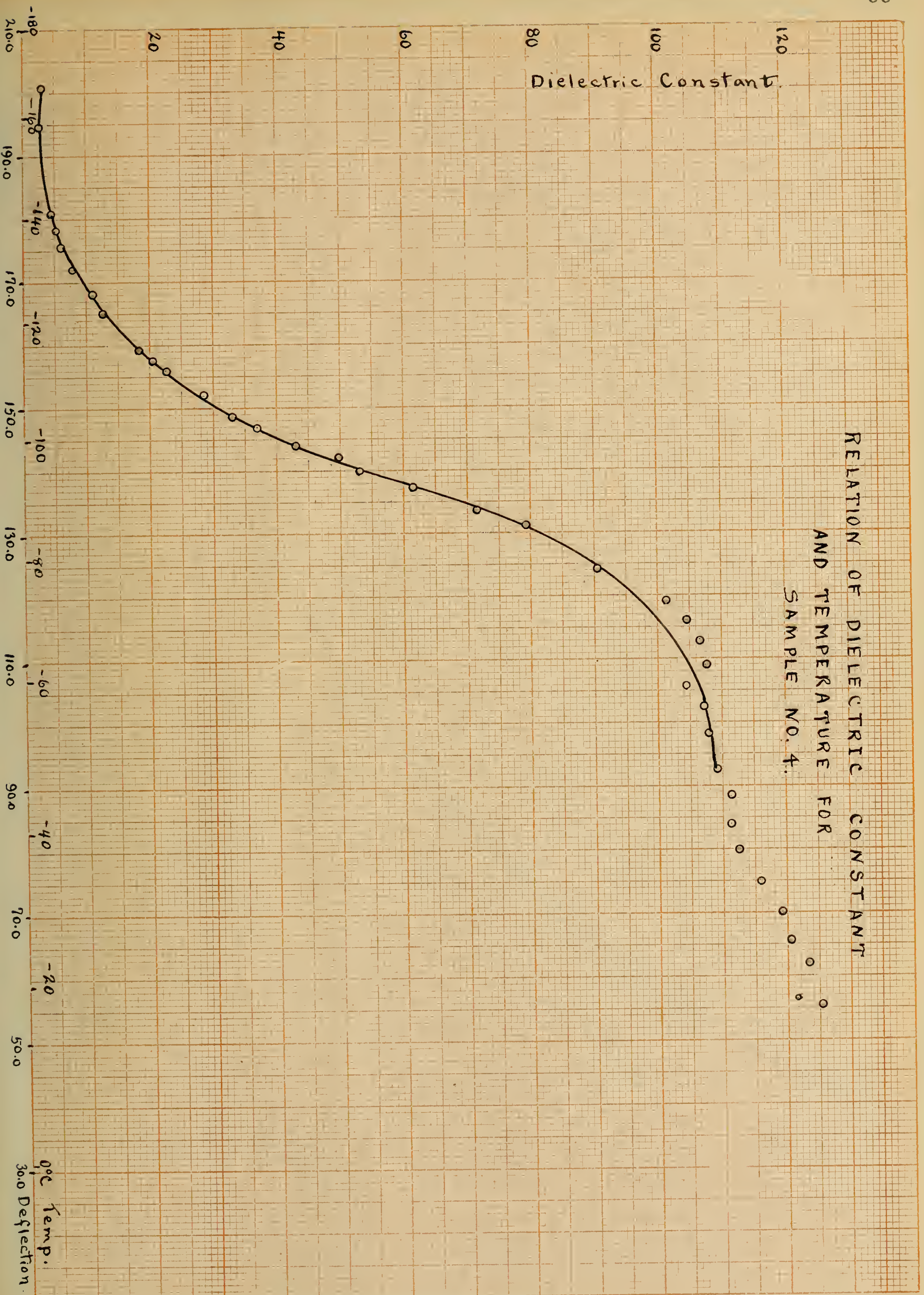
Zero reads 22.72 at 7:20 but is slowly drifting until it is 22.80 at 7:24. The true zero was taken as 23.00

32.20 (23.00)	122.00	57.0	7:33
R13.48 (23.00)	126.27	55.5	7:37

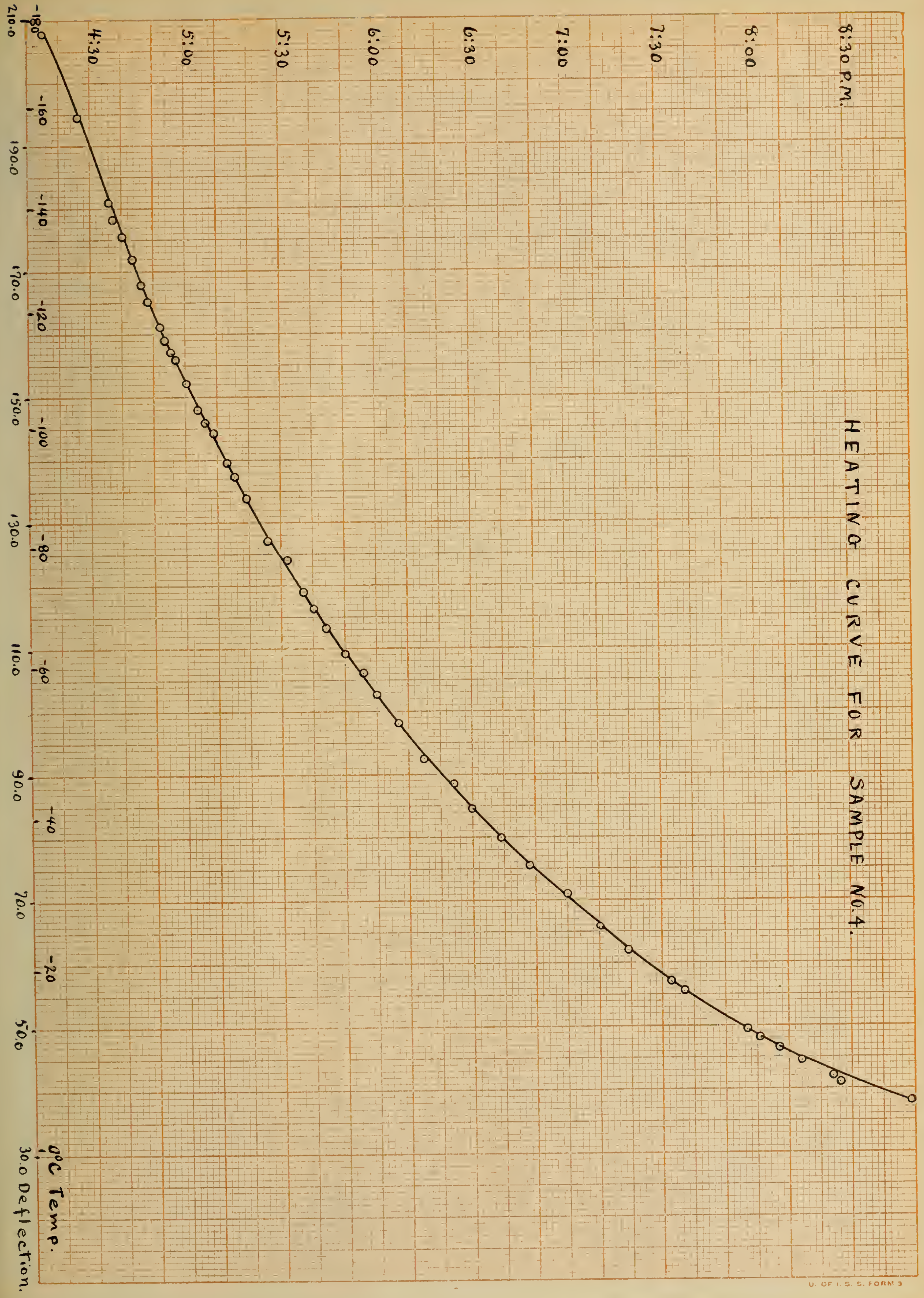
Zero reads 22.68 but is drifting toward 23.00

33.70 (23.00)	150.26	49.5	7:57
R10.50 ?? (23.00)	166.08	48.1	8:01
34.62 (23.00)	154.32	46.6	8:07
Deflection off the scale		32.8	9:10

Examination of condenser showed that the ice was beginning to melt on the top of the inner cone, and that the layer of ice between the two cones was badly checked.



U OF I S S FORM 3


HEATING CURVE FOR SAMPLE NO.4.
4:30
5:00
5:30
6:00
6:30
7:00
7:30
8:00
8:30 P.M.
-180
-160
-140
-120
-100
-80
-60
-40
-20
0°C Temp.
210.0
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
30.0 Deflection.
U. OF I. S. S. FORM 3

Sample No. 5

Charging voltage 20.62 Warm junction of thermo-couple 21°C

Galvanometer shunt 50 ohms

Reading due to air condenser, leads and commutator		24.32	
Zero reading		23.00	
	Deflection	1.32	
Reading due to air condenser, leads and commutator		R21.70	
Zero reading		23.00	
	Deflection	1.30	
	Average		1.31
Reading due to leads and commutator		23.59	
Zero reading		23.01	
		.58	
Reading due to leads and commutators		R22.43	
Zero reading		23.01	
	Deflection	.58	
	Average		.58

Deflection due to air condenser = 1.31 - .58 = .73

Galvanometer shunt 20 ohms

Reading due to air condenser, leads and commutator		23.58	
Zero reading		23.00	
	Deflection	.58	
Reading due to air condenser leads and commutator		R22.42	
Zero reading		23.00	
	Deflection	.58	
	Average		.58

Reading due to leads and commutators 23.27

Zero reading 23.00

Deflection .27

Reading due to leads and commutator R22.74

Zero reading 23.00

Deflection .26

Average .265

Deflection due to air condenser = .58 - .265 = .315

Condenser taken out of liquid air at 5:53P.M., and wrapped in canton flannel and then packed in the broken Dewar cylinder.

Galvanometer shunt 50 ohms

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
25.92 (23.00)	3.21	196.2	5:55P.M.
26.00 (23.00)	3.31	185.8	6:03

Frequency: 1000 revolutions per 36 seconds

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
26.41 (23.00)	3.88	179.2	6:09
R19.50 (23.00)	4.00	177.5	6:11
26.90 (23.02)	4.52	174.5	6:14
R19.05 (23.02)	4.64	173.5	6:15
27.50 (23.02)	5.34	170.5	6:19
R18.00 (23.02)	6.03	168.2	6:21
29.15 (23.00)	7.63	165.0	6:25

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
R16.20 (23.00)	8.52	162.7	6:27P.M.
Frequency: 1000 revolutions per 36 seconds			
30.90 (23.00)	10.02	160.1	6:31
R13.70 (23.00)	11.94	157.0	6:35
33.70 (23.00)	13.86	154.2	6:38
R9.80 (23.00)	17.29	150.4	6:43
39.00 (23.07)	21.43	146.7	6:48
R2.00 (23.02)	28.14	143.5	6:52
Voltage changed to 4.15			
28.00 (23.03)	33.04	140.3	6:57
R17.00 (23.03)	40.26	136.7	7:02
Frequency: 1000 revolutions per 36 seconds			
29.90 (23.03)	45.97	134.2	7:06
5000 ohms does not change deflection			
R15.00 (23.03)	53.88	131.7	7:10
32.10 (23.03)	60.96	129.0	7:13
34.16 (23.01)	75.12	125.0	7:20
R10.90 (23.01)	81.66	122.0	7:25
36.40 (23.01)	90.37	118.0	7:31

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
R8.60 (23.01)	97.31	113.4	7:39P.M.
37.70 (23.06)	98.87	110.5	7:44
R7.55 (23.06)	104.79	106.5	7:51
Drift of zero just noticeable			
R7.20 (23.06)	107.18	102.6	7:59
38.70 (23.06)	105.68	9.98	8:05
R7.12 (23.06) 5000 ohms changed reading to 7.2	108.52	9.50	8:14
38.90 (23.00) 5000 ohms changes reading to 38.80 The zero drifts as follows; 23,22 at 8:23, 23.10 at 8:26, 23.08 at 8:28	107.45	91.5	8:21
R6.52 (23.00)	111.40	85.2	8:35
39.40 (23.00)	110.83	83.1	8:39
39.40 (23.00)	110.83	77.2	8:53
R6.40 (23.00)	112.22	75.5	8:59
Voltage changed to 2.09			
Galvanometer shunt changed to 20 ohms			
26.48 (23.00)	109.14	71.9	9:08
R19.45 (23.00) 5000 ohms changes reading to 19.49	111.34	70.6	9:11

The drift of the zero is very noticeable

Reading of Galvanometer when Ice is the Dielectric	Dielectric Constant	Deflection of thermo-couple Galvanometer	Time
22.62 (23.00)	113.56	67.3	9:20P.M.
26.72 (23.00)	113.88	62.1	9:35

Five minutes after breaking the switch the actual zero reading was 23.05, but slowly changing toward 23.00

R21.90 (23.00)	33.97	58.2	9:46

The galvanometer moves by jerks!

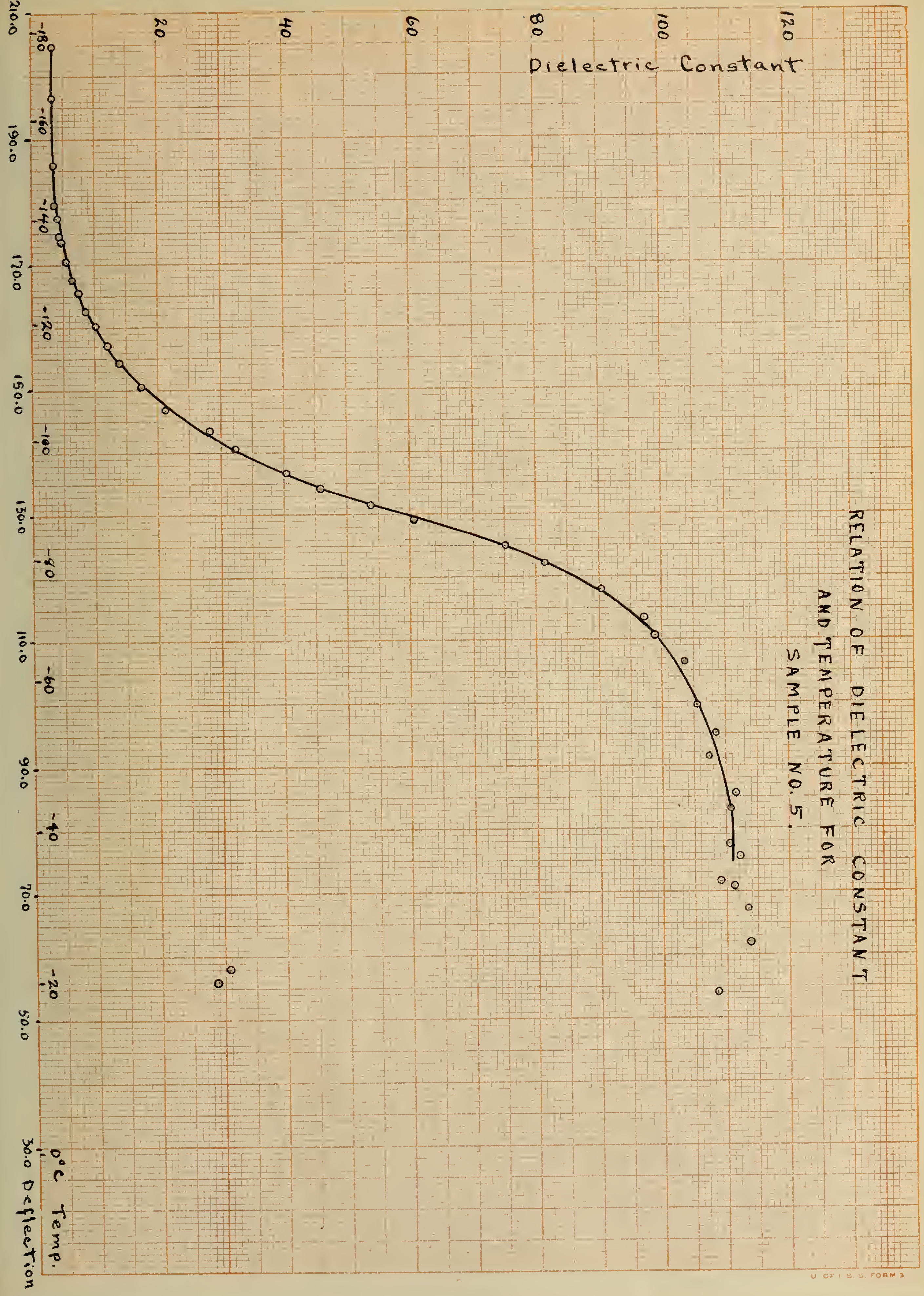
24.00 (23.00)	30.80	58.0	9:47

Galvanometer shunt changed back to 50 ohms

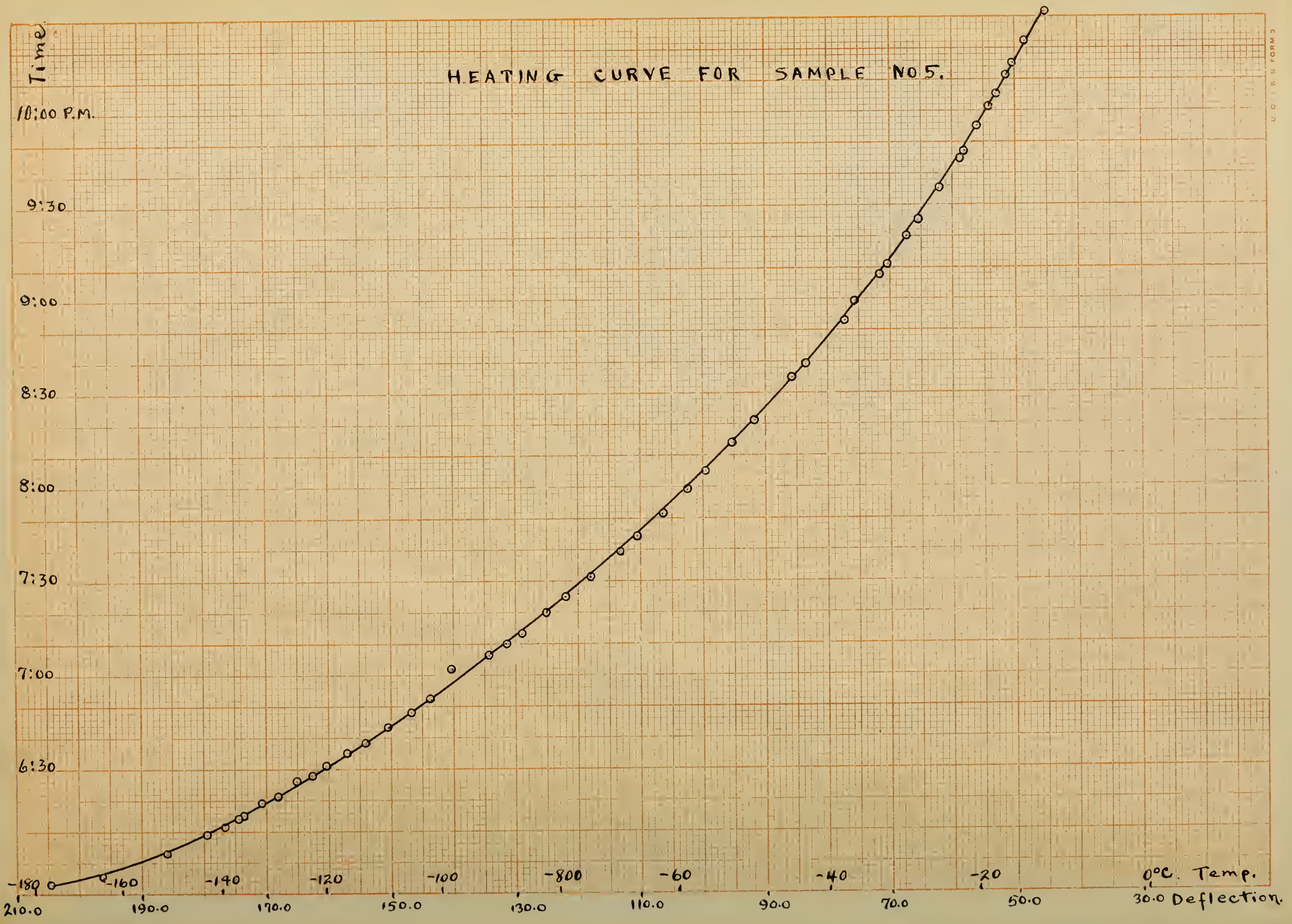
25.20 (23.00)	28.99	56.0	9:55
R14.90 (23.00)	108.73	54.0	10:01

Reflections so unsteady that they can not be read

Inspection of the condenser showed that the ice between the walls was badly checked and that the condensed moisture had collected on the connecting wires and upon the ebonite insulation.



RELATION OF DIELECTRIC CONSTANT AND TEMPERATURE FOR SAMPLE NO. 5.



HEATING CURVE FOR SAMPLE No 5.

VIII DISCUSSION OF RESULTS

All the samples used in this experimental work were obtained from distilled rain water. The distillation was carried on in the open air and no special precautions taken to insure great purity.

The general shape of the curves show that the work is a verification of that done by Fleming and Dewar[80] and that the dielectric constant of ice at liquid air temperatures is approximately 3. As found by these authors slight impurities have a remarkable effect on the shape of the curve particularly at about -100°C. Although all samples were prepared in the same way still no two curves will be found to coincide exactly. Taken in connection with the work of Abegg and Palmer the curves show that at some temperature between that of liquid air and melting ice there is a distinct maximum and hence that ice may have the same dielectric constant at two very different temperatures.

It was found impossible to run the curves much above -60°C as the conductivity of the ice at that temperature became considerable. Further, the erratic action of the galvanometer and the exceedingly slow return to zero indicated that an electrolytic cell had been formed due to the electrolytic action of the conduction current. This conclusion was supported by the fact that on breaking the charging circuit the return to zero was always from the direction of the last deflection. It did not appear to be due to a residual discharge as one would suppose from the work of Hopkinson and Wilson[81], as it is only experienced after the ice has become conducting and is more

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[80] J. A. Fleming and J. Dewar, Proc. Roy. Soc., Vol.61,p.316,(1897)

[81] J. Hopkinson and E. Wilson, Phil.Trans.,Ser.A.,Vol.189,p134,(1897)

marked the greater the conductivity.

It is hoped that the above investigation will be continued, working on a sample of the purest water available and using a platinum plate condenser excluded from the air by being enclosed in a glass vessel. Perhaps a good model would be that described by Eversheim in his work on the dielectric constant of liquid sulphur dioxide.

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